AGE DATING GROUND WATER BY USE OF CHLOROFLUOROCARBONS (CCl₃F AND CCl₂F₂), AND DISTRIBUTION OF CHLOROFLUOROCARBONS IN THE UNSATURATED ZONE, SNAKE RIVER PLAIN AQUIFER, IDAHO NATIONAL ENGINEERING LABORATORY, IDAHO

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CONTENTS

			Page
Abstract	t		1
Introdu	ction		2
Purp	ose a	nd Scope	3
Geoh	ydro	logic setting	3
Method	s of s	tudy	6
Colle	ction	and analysis of ground-water samples for nitrogen, oxygen, argon,	
an	nd car	bon dioxide	6
Colle	ection	and analysis of ground-water and soil-gas samples for	
ch	lorof	luorocarbons	6
Estin	natio	n of recharge-water temperature	7
Selected	l chai	acteristics of ground water	10
Disso	olved-	gas content	10
Chlor	roflu	procarbon content	14
Age dati	ing g	round water by use of chlorofluorocarbons	18
Reco	nstru	ction of the chlorofluorocarbon concentrations in the atmosphere	18
Chlor	roflu	procarbon-model ages of recharge	21
Unce	ertain	ties in chlorofluorocarbon-model recharge ages of old and young	
gr	ound	water	22
Grou	ınd w	aters contaminated with chlorofluorocarbons	25
Age o	of rec	harge at the Idaho National Engineering Laboratory	29
Distribu	ıtion	of chlorofluorocarbons in the unsaturated zone	31
Radio	oactiv	ve Waste Management Complex	31
Test	Area	North	33
Summa	ry an	d conclusions	40
Referen	ces ci	ted	41
		ILLUSTRATIONS	
Figure	1.	Location of the Idaho National Engineering Laboratory and selected	
		facilities	5
	2.	Dissolved nitrogen and argon compositions of ground waters collected at	
		and near Idaho National Engineering Laboratory	13

			Page
	3.	Concentrations of chlorofluorocarbon-11, and chlorofluorocarbon-12 in	00
	4.	the atmosphere	20
	_	Laboratory and vicinity	27
	5.	Locations of selected wells and model chlorofluorocarbon-11 and chlorofluorocarbon-12 recharge dates, Test Reactors Area and Radioactive Waste Management Complex	28
	6.	Measured and simulated concentrations of chlorofluorocarbon-11 and chlorofluorocarbon-12 with depth in the unsaturated zone at an instal-	20
		lation near Test Area North at Idaho National Engineering Laboratory	39
		TABLES	
Table	1.	Dissolved-gas compositions of ground waters	11
	2.	$Well \ construction \ and \ water \ levels \ at \ the \ time \ of \ sampling, \ Idaho\ National$	
	n	Engineering Laboratory, Idaho	12
	3.	Concentrations of dissolved chlorofluorocarbon-11 and chlorofluorocarbon-12 in ground waters from Idaho National Engineering Laboratory,	
		Idaho	15
	4.	Yearly average concentrations of chlorofluorocarbon-11 and chlorofluorocarbon-12 in the atmosphere	19
	5.	The effects recharge of temperature on the model chlorofluorocarbon dates	
	6.	The effects of elevation on the model chlorofluorocarbon dates	
	7.	Concentrations of chlorofluorocarbon-11 and chlorofluorocarbon-12 in the unsaturated zone at Idaho National Engineering Laboratory,	
	0	Idaho	32
	8.	Molecular diffusion constant for the diffusion of gas A into gas B (D_{AB}), liquid partitioning coefficients (K_w), and sorptivity to geologic materials	0.0
	9.	(K_s) of chlorofluorocarbon-11 and chlorofluorocarbon-12	36
		(τ), given as a function of depth and geologic material	37

CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	<u>To obtain</u>
millimeter (mm)	3.937×10^{-2}	inch
centimeter (cm)	3.937×10^{-1}	inch
meter (m)	3.281×10^{0}	foot
kilometer (km)	6.214 X 10 ⁻¹	mile
square centimeter (cm²)	1.550 X 10 ⁻¹	square inch
square kilometer (km²)	3.861 X 10 ⁻¹	square mile
cubic centimeter (cm³)	6.102 X 10 ⁻²	cubic inch
cubic meter (m³)	3.531×10^{1}	cubic foot
milliliter (mL)	6.102 X 10 ⁻²	cubic inch
liter (L)	2.642 X 10 ⁻¹	gallon
picogram (pg)	3.527×10^{-14}	ounce
gram (g)	2.205 X 10 ⁻³	pound
kilogram (kg)	2.205×10^{0}	pound
kilopascal (kPa)	$6.895 \ \mathrm{X} \ 10^{\mathrm{0}}$	pound per square inch

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$^{\circ}F = 1.8(^{\circ}C) + 32$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviated water-quality units used in this report: Chemical concentrations of constituents dissolved in water are given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Specific conductance of water is expressed in microsiemens per centimeter at 25 degrees Celsius (µS/cm).

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ABSTRACT

Detectable concentrations of chlorofluorocarbons (CFC's) were observed in ground water and unsaturated-zone air at the Idaho National Engineering Laboratory (INEL) and vicinity. The recharge ages of waters were determined to be from 4 to more than 50 years on the basis of CFC concentrations and other environmental data; most ground waters have ages of 14 to 30 years. These results indicate that young ground water was added at various locations to the older regional ground water (greater than 50 years) within and outside the INEL boundaries. The wells drilled into the Snake River Plain aquifer at INEL sampled mainly this local recharge. The Big Lost River, Birch Creek, the Little Lost River, and the Mud Lake-Terreton area appear to be major sources of recharge of the Snake River Plain aquifer at INEL.

An average recharge temperature of $9.7\pm1.3^{\circ}C$ (degrees Celsius) was calculated from dissolved nitrogen and argon concentrations in the ground waters, a temperature that is similar to the mean annual soil temperature of $9^{\circ}C$ measured at INEL. This similarity indicates that the aquifer was recharged at INEL and not at higher elevations that would have cooler soil temperatures than INEL.

Soil-gas concentrations at Test Area North (TAN) are explained by diffusion theory. The measured difference between apparent ages based on CFC-11 and CFC-12 concentrations is 7.5 years for the soil atmosphere near the water table at TAN. If ground-water recharged by slow percolation through the unsaturated zone, CFC concentrations in water would be in equilibrium with the unsaturated zone and would have apparent CFC-11 ages that are older than CFC-12 ages by a few years. Most of the ground water sampled in the vicinity of INEL indicates that the CFC-11- and CFC-12-based ages are nearly identical and not in equilibrium with the deep

unsaturated-zone air. These observations indicate that the ground waters equilibrated near or within the thin soil-zone and then moved rapidly through the fractured basalts to the water table without gas-water reequilibration.

Ground waters near and southwest of the Radioactive Waste Management Complex (RWMC), the Test Reactor Area (TRA), and the Idaho Chemical Processing Plant (ICPP) contain levels of CFC's that are indicative of contamination. The CFC data indicate that a large CFC-12 waste plume may originate in the vicinity of TRA. The areal extent of the CFC-12 waste plume may resemble the previously documented tritium ground-water plume; however, the CFC-12 plume seems to be larger.

Measurements at TAN show no CFC contamination of the unsaturated zone. The results are consistent with the movement of CFC's from the atmosphere into the unsaturated zone by gaseous diffusion. The measured concentration of CFC's in ambient air at this site indicate no contamination with CFC's. Air piezometers near the RWMC indicate that concentrations of CFC's are tens of times greater than those of 1991 air. Because the concentrations of CFC's increased with depth, it appears the source of the CFC's may be the 34 m and 73 m sedimentary interbeds. Calculations indicate that the flux of CFC-11 is from the unsaturated-zone atmosphere into the ground water. Anomalously high concentrations of CFC's were measured in an air sample collected at this site, which indicate a possibly significant flux of CFC's from the unsaturated zone into the atmosphere near the RWMC.

INTRODUCTION

Chlorofluorocarbons (CFC's or Freons¹) are stable synthetic organic compounds that are detectable to about one part in 10^{15} (weight) in water and one part in 10^{12} (volume) in air. CFC's were first manufactured in the 1930's, and they are entirely of anthropogenic origin (Lovelock, 1971). Two chlorofluoromethanes--trichlorofluoromethane (CCl₃F, CFC-11, Freon-11, F-11) and dichlorodifluoromethane (CCl₂F₂, CFC-12, Freon-12, F-12)--make up 77 percent of total CFC global production (Derra, 1990). CFC's are ultimately released into the atmosphere and hydrosphere. The concentrations of CFC's in surface water vary as a function of atmospheric partial pressure of CFC's and temperature of the water.

The use of CFC concentrations in natural waters as a potential dating tool was recognized in the mid-1970's. Detectable concentrations of CFC's are present in post-1940 ground water. The presence of CFC's in ground water indicates recharge after 1940 or mixing of older waters with post-1940 water. Thompson (1976) and Thompson and Hayes (1979) measured the CFC-11

¹ The use of trade or product names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

content of ground waters from southern New Jersey, Arkansas, and south-central Texas. Their results were in qualitative agreement with the hydrology and tritium concentrations in those three localities. Recently, CFC-11 and CFC-12 were used to date ground waters from Long Island, N. Y. (Epler, 1990). CFC ages were found to be consistent with distributions of aldicarb, a pesticide that was first introduced in 1975. CFC's have been used extensively to date ground waters in central Oklahoma (Busenberg and Plummer, 1991; 1992) and in the Delmarva Peninsula of Maryland, Delaware, and Virginia (L. N. Plummer and E. Busenberg, U.S. Geological Survey, unpub. data). The results of these two studies are in close agreement with the hydrology, and the distributions of nitrate, herbicides, and tritium concentrations in the samples.

In 1949, the U.S. Atomic Energy Commission, later to become the U.S. Department of Energy, requested that the U.S. Geological Survey investigate the water resources of Idaho National Engineering Laboratory (INEL) and adjacent areas in south eastern Idaho to describe the geochemistry of the ground water and to delineate the movement of facility-related chemical wastes in the Snake River Plain aquifer. As part of this investigative program, ground water in the Snake River Plain aquifer was sampled for CFC's within and in the vicinity of INEL on two separate occasions in May and July 1991. In addition, 15 Idaho wells were sampled and the waters analyzed for dissolved N₂, O₂, Ar, CO₂, and CH₄ concentrations. The main purpose of this study was to determine whether the concentrations of the CFC's in waters can be used to date the recharge to the Snake River Plain aquifer at INEL. Another purpose for this study was to investigate the possibility of using CFC's to delineate the movement of organic chemicals in the aquifer and unsaturated zone. The samples were collected and analyzed by the U.S. Geological Survey in cooperation with the U.S. Department of Energy.

Purpose and Scope

This report describes the distribution and concentrations of CFC's in ground waters at INEL and vicinity. The results of more than 140 CFC analyses of ground water from 24 wells and 14 CFC analyses of unsaturated-zone gases from 6 wells at INEL are presented and interpreted. The report also describes the distribution of CFC's in the unsaturated zone at Test Area North (TAN) and in the vicinity of the Radioactive Waste Management Complex (RWMC). A brief summary of field and laboratory procedures is presented, followed by an evaluation of the gas-recharge temperatures, and the CFC model-recharge ages.

Geohydrologic Setting

The eastern Snake River Plain is a northeast-trending structural basin about 320 km long and 80 to 110 km wide. The plain is underlain by a layered sequence of basaltic lava flows and cinder beds interbedded with eolian, fluvial, and lacustrine sedimentary deposits. The thickness

of individual flows generally ranges from 3 to 15 m, and the average thickness may be from 6 to 7.5 m (Mundorff and others, 1964, p. 143). The sedimentary deposits consist mainly of beds of sand, silt, clay, and lesser amounts of gravel. Locally, rhyolitic lava flows and tuffs are exposed at land surface or are present at depth. The basaltic lava flows and interbedded sedimentary deposits combine to form the Snake River Plain aquifer, which is the main source of water on the plain.

Recharge to the Snake River Plain aquifer is principally from infiltration of applied irrigation water, infiltration of streamflow, and ground-water inflow from the alluvium of adjoining mountain drainage basins. Some recharge may be from direct infiltration of precipitation, although the small annual precipitation on the plain (20 cm at INEL), evapotranspiration, and the great depth to water (in places exceeding 275 m) probably minimize this source of recharge (Orr and Cecil, 1991, p. 22-23).

The Big Lost River drains more than 3,600 km² of mountainous area that includes parts of the Lost River Range and the Pioneer Range west of INEL (fig. 1). Flow in the Big Lost River infiltrates to the Snake River Plain aquifer along its channel and at sinks and playas. Since 1958, excess runoff has been diverted to spreading areas in the southwestern part of INEL, where much of the water rapidly infiltrates to the aquifer. Other surface drainage that provides recharge to the Snake River Plain aquifer at INEL includes Birch Creek and the Little Lost River (fig. 1) (Orr and Cecil, 1991, p. 23).

Water in the Snake River Plain aquifer moves principally through fractures and interflow zones in the basalt. A significant proportion of ground water moves through the upper 240 m of saturated rocks (Mann, 1986, p. 21). Hydraulic conductivity of basalt in the upper 240 m of the aquifer generally is 0.3 to 30 m·day-1. Hydraulic conductivity of underlying rocks is several orders of magnitude smaller. The effective base of the Snake River Plain aquifer at INEL probably ranges from 260 to 370 m below land surface (Orr and Cecil, 1991, p. 25).

At INEL, depth to water in wells completed in the Snake River Plain aquifer ranges from about 60 m at the northern part to more than 275 m in the southeastern part. The direction of ground water flow within the aquifer is mainly southward and southwestward at an average hydraulic gradient of about 0.7 m·km⁻¹. Ground water moves southwestward from INEL and eventually discharges to springs along the Snake River downstream from Twin Falls, about 160 km southwest of INEL (Orr and Cecil, 1991, p. 25).

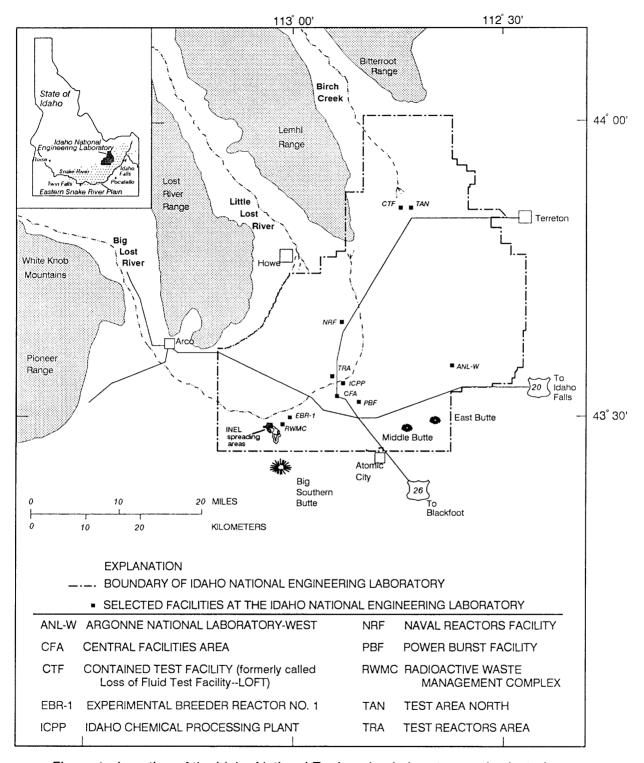


Figure 1.--Location of the Idaho National Engineering Laboratory and selected facilities.

METHODS OF STUDY

In this section are described the specialized apparatus and procedures that are needed to collect and analyze ground waters and soil gases for nitrogen (N_2) , oxygen (O_2) , carbon dioxide (CO_2) , argon (Ar), methane (CH_4) , and chlorofluorocarbons.

Collection and Analysis of Ground-Water Samples for Nitrogen, Oxygen, Carbon Dioxide, Argon, and Methane

The sampling apparatus for dissolved gases is illustrated and described in detail elsewhere (Hobba and others, 1977; Pearson and others, 1978). Briefly, the apparatus consists of a water chamber and a sidearm that was evacuated before sampling. The 500-mL water chamber was connected to the well with flexible tubing. The water chamber was filled with well water. The upward flow of water through the water chamber completely displaced and removed all the air. After the chamber was thoroughly flushed, it was sealed to the atmosphere. The water chamber was then opened to the evacuated 50-mL sidearm.

The sampling apparatus was allowed to equilibrate at room temperature for several days. The sampler was then connected to a gas chromatographic system. The pressure within the sidearm was measured with a pressure transducer. Headspace gas was then injected into the gas chromatograph to measure N_2 , O_2 , CO_2 , Ar, and CH_4 composition of the dissolved gases. The gas chromatography system was calibrated with several gas standards. The concentrations of gases in the aqueous phase of the water chamber can be calculated from the water-sample temperature by means of Henry's law (Wilhem and others, 1977; Warner and Weiss, 1985). From the temperature, the pressure in the sidearm, the volumes of the water chamber and sidearm, the gas law, and the concentrations, the amounts present in the two phases can be calculated. The concentration in the aquifer is the sum of the amounts present in the two phases divided by the volume of the water chamber.

Collection and Analysis of Ground-Water and Soil-Gas Samples for Chlorofluorocarbons

From 3 to more than 20 CFC samples were collected at each well, and at least 3 samples were analyzed from each of the 24 wells sampled in Idaho. The sampling procedure consisted of (1) purging three borehole volumes; (2) monitoring the field measurements of pH, dissolved O₂, specific conductance, and temperature; and (3) sampling for CFC's after the field-measurements stabilized. The wells were connected to the sampling apparatus with an aluminum tube to prevent contamination with air (Reynolds and others, 1990). The water samples

were collected in 62-mL borosilicate glass ampules and preserved in the field by sealing without contact with the atmosphere. The apparatus for collecting and sealing water samples in the ampules and other details of the field procedures are given in Busenberg and Plummer (1992).

Gas samples from the unsaturated zone were collected in stainless-steel cylinders and 100-mL borosilicate glass ampules. The cylinders were fitted with inflow and outflow stainless-steel bellows valves, which allowed the flushing of the samplers containing the gas samples. The cylinders were filled with pressurized CFC-free N_2 when not in use. The procedures used for collecting gas samples in cylinders have been described in detail by Thompson and others (1985). Unsaturated zone gas wells were first purged by use of an ultraclean stainless-steel pump. After purging, the gas flow was switched to the cylinder by means of a three-way valve. The ultrapure N_2 in the cylinder was released by opening the outflow valve. The inflow valve was opened, allowing the unsaturated-zone gas to flow through the cylinder for several minutes. The outflow valve was then closed, and pumping was continued to pressurize the cylinder to about 2 atmospheres before the inflow valve was closed. The gas samples in the glass ampules were collected with an apparatus very similar to the one used for collecting ground-water samples (Busenberg and Plummer, 1992). After being purged, the ampules were sealed by fusing the necks with a torch.

CFC's in ground water were determined in the laboratory by use of a purge-and-trap gas chromatography procedure with an electron capture detector (ECD). In brief, the sample was introduced into a stripping chamber, and the CFC's were purged with ultrapure N_2 and quantitatively collected in a trap cooled to -30°C. The CFC's were released when the trap was heated to 95°C. CFC-11 and CFC-12 were separated from other halocarbons in a precolumn. After CFC-11 and CFC-12 entered the analytical column, the precolumn was back flushed to remove all other highly retentive halocarbons. The concentrations of CFC-11 and CFC-12 in the aquifer were calculated from the concentrations in the water sample, the water-sample temperature, and the volumes of water and headspace in the ampules. A detailed description of the procedures can be found in Busenberg and Plummer (1992).

Gas samples were loaded into sampling loops, injected into the instrument, and collected on a trap cooled to -30°C; after this point, the procedure was identical to that for water samples (Busenberg and Plummer, 1992).

Estimation of Recharge-Water Temperature

Numerous studies have found that noble gases and N₂ solubilities are excellent indicators of recharge-water temperature (Heaton, 1981; Heaton and Vogel, 1981; Andrews and others, 1985; Mazor, 1972; Herzberg and Mazor, 1979; Andrews and Lee, 1979). Often, temperatures

derived from gas solubilities are nearly the same as the mean annual air temperatures because the unsaturated-zone temperatures a few meters below the ground surface do not vary and reflect the mean annual air temperature (Heaton and others, 1986).

Recharge-water temperatures were determined from the concentrations of dissolved N_2 and Ar in ground water. The equilibrium solubilities of gases in water are described by Henry's law,

$$K_{i} = \frac{C_{i}}{P_{i}}, \tag{1}$$

where K_i is Henry's law constant for the i^{th} gas,

 C_i is the concentration of the i^{th} gas in solution, and

 $P_{\rm i}$ is the partial pressure of the gas.

The solubilities of gases vary significantly as a function of temperature; therefore, the dissolved-gas composition of the ground water reflects the temperature of the unsaturated zone. The temperature dependence of K_i for N_2 , O_2 , and A_1 has been carefully evaluated by Weiss (1970) and for CFC-11 and CFC-12 by Warner and Weiss (1985).

Detailed studies of N₂ and noble-gas solubilities have shown that air bubbles can be transported into the saturated zone and that the bubbles eventually dissolve because of the hydrostatic pressure, resulting in "excess air" (Heaton, 1981; Heaton and Vogel, 1981; Andrews and others, 1985). The amount of excess air introduced into ground water is determined by the physical nature of the capillary fringe just above the saturated zone. The formation of bubbles and their entrapment is favored in fine-grained sediments and by some flow conditions in fractured rocks, but bubbles are less likely to form in coarse sediments or in rocks with wide joints (Heaton, 1981; Heaton and Vogel, 1981; Andrews and others, 1989). Heaton and Vogel (1981) have shown that climate also can influence the amount of excess air introduced into ground water. Occasional significant rain storms in semiarid areas cause a rapid rise in the water table and the entrapment of air bubbles, resulting in large excess-air values. (Heaton and Vogel, 1981). Presence of excess air is easily identified because the N₂:Ar ratios in air and in solution that is in equilibrium with air are about 30 and 80, respectively.

Ground water below the water table tends to preserve the dissolved-gas composition; however, various processes are known to change the dissolved-gas composition acquired in the unsaturated zone. If upward or downward concentration gradients exist within the aquifer,

small changes could take place through diffusive movement; estimates of these diffusive losses or gains are small compared to the total amount present for the major gas constituents of air (Heaton and others, 1986).

Dissolved O_2 is easily consumed by biological processes and cannot be used in the evaluation of recharge temperatures. N_2 concentrations in ground water can be modified by the microbial reduction of NO_3 - to N_2 in anoxic ground waters (Heaton and others, 1981; 1983). The dissolved N_2 in water can be derived from different sources, as follows:

$$N_{2 TD} = N_{2 WEA} + N_{2 EA} + N_{2 DN},$$
 (2)

where N_{2TD} is the total dissolved N_2 in the ground water;

 $N_{2 WEA}$ is the N_2 introduced as a result of the water-air equilibrium in the unsaturated zone;

 N_{2EA} is the N_2 derived from dissolution of excess air; and

 $N_{2\,DN}$ is the N_2 formed by the denitrification of fixed nitrogen in anoxic ground waters.

Although Ar is chemically inert, its concentration can be modified by the presence of excess air and radiogenic Ar. Radiogenic Ar, produced by the radioactive decay of ⁴⁰K, is of little importance even in old waters because (1) the rates of production are small and (2) most of the radiogenic Ar is retained in the rocks (Podosek and others, 1980; Heaton and others, 1983). The total dissolved Ar in ground water is given by the equation

$$Ar_{TD} = Ar_{WEA} + Ar_{EA} + Ar_{RD}, \tag{3}$$

where Ar_{TD} is the total dissolved Ar in the ground water;

 Ar_{WEA} is the Ar introduced as a result of the water-air equilibrium in the unsaturated zone;

 Ar_{EA} is the Ar derived from the dissolution of excess air; and

 Ar_{RD} is the Ar produced by radioactive decay of $^{40}\mathrm{K}$ and released into the ground water.

Only small quantities of Ar are produced by radiogenic decay of 40 K in rocks, and only a small part of the radiogenic Ar is released from the minerals into ground water, as compared to the substantial amount of the radiogenic He that is released into ground water (Podosek and others, 1980). The Ar_{RD} has been found to be proportional to the radiogenic concentrations of He_{RD} in some ground waters, as follows:

$$Ar_{RD} = k \cdot He_{RD}, \tag{3}$$

where k is a constant. Heaton and others, (1983) used a value of 0.14 for k in South African sedimentary rocks. The value of k can be smaller (Podosek and others, 1980) or in some cases larger than 0.14 (Mazor, 1977).

The equilibrium concentrations of dissolved gases are proportional to their atmospheric partial pressures (eq 1). The barometric pressure decreases with elevation; even though the mole fractions of the various gases remain constant, their partial pressures decrease with increasing elevation and, therefore, the equilibrium solubilities of the gases decrease. The equations describing changes in barometric pressure as a function of geometric height and tables of the U.S. Standard Atmosphere are given by the Committee on Extension to the Standard Atmosphere (1976).

Elevation significantly affects the calculated recharge-water temperature. The effect of barometric pressure for an elevation of about 210 m above sea level is equivalent to 1°C in calculated recharge-water temperature. The elevation of recharge water should be known or accurately estimated before gas solubilities are used to evaluate recharge-water temperatures.

SELECTED CHARACTERISTICS OF GROUND WATERS

Ground waters from 15 Idaho wells were sampled for dissolved gases (table 1). Nine of these wells are located at or near INEL; the rest of the wells are in mountain valleys north and northwest of INEL. In addition, the concentrations of CFC-11 and CFC-12 were measured in the more than 140 ground-water samples collected from 24 wells (table 2) within and outside the boundaries of INEL.

Dissolved-Gas Content

The measured concentrations of dissolved N_2 , O_2 , Ar, CO_2 , and CH_4 in nine of the Idaho ground waters are given in table 1. The recharge-water temperatures and amounts of excess air can be evaluated from plots of dissolved N_2 against Ar concentrations. If the measured gas concentrations were used, a separate graph would be required for each recharge elevation. This problem was overcome by normalizing the observed N_2 and Ar concentrations to 760 mm Hg

barometric pressure by use of the U.S. Standard Atmosphere tables (Committee on Extension to the Standard Atmosphere, 1976). In figure 2, the x-axis and y-axis represent the normalized concentrations of the N_2 and Ar in the water. The zero-excess-air line represents the solubility of the two gases between 0 and 30°C at sea level. The 5, 10, 15 and 20 lines represent their equilibrium concentrations with 5, 10, 15, and 20 cm³·L⁻¹ of air added in excess of the equilibrium concentrations, respectively.

On the lower right hand corner of figure 2 are shown the evolution of the dissolved gases of a water. Addition of radiogenic Ar will shift the sample composition (filled circle) vertically as shown. Bacterial reduction of nitrate to N_2 will shift the dissolved-gas composition horizontally. Addition of excess air will shift the composition diagonally. The slope of the line is determined by the N_2 to Ar ratio in air. With the exception of two samples (wells 87 and 117), all the deviations from the water in equilibrium with air (WEA) or zero-excess-air line, are caused by the presence of excess air. The recharge-water temperature of a sample on the diagram can be obtained by following a diagonal line (parallel to the temperature lines) from the sample to the recharge-water-temperature axis. The excess-air content of the sample can be obtained by following a diagonal line (parallel to the excess-air lines) from the sample to the excess-air axis. In addition to the recharge-water temperature, these diagrams provide valuable information on the recharge mechanism of ground waters (Mazor and Verhagen, 1983; 1984).

 ${\bf Table\,1.\text{--}Dissolved-gas\,compositions\,of\,ground\,waters,Idaho\,National\,Engineering\,Laboratory,}\\ {\bf Idaho\,}$

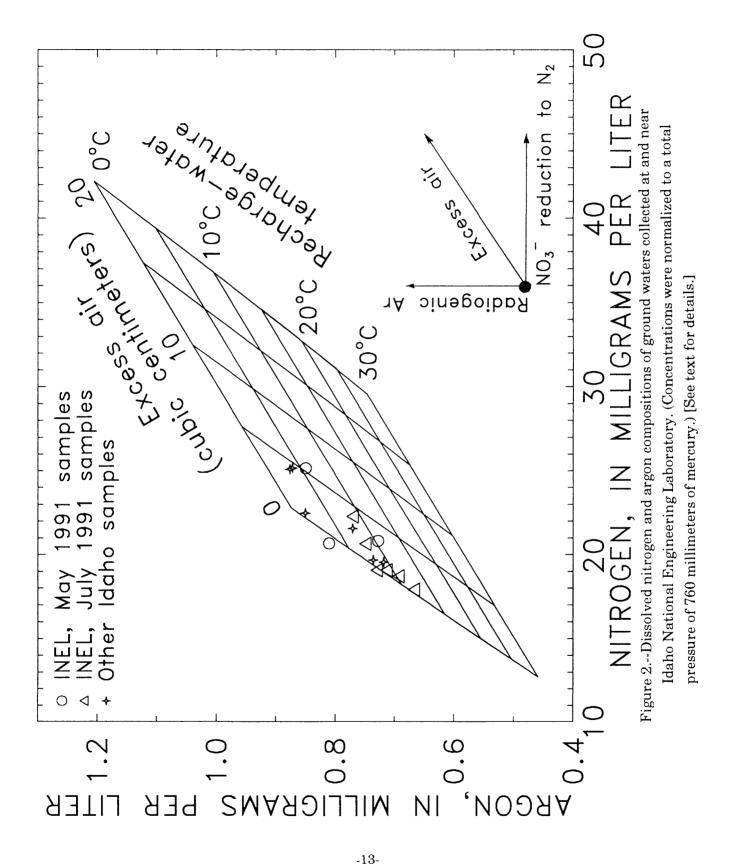
[Gas concentrations are in milligrams per liter. Sampling dates are given as month/day/year]

Well name	Sampling date	N_2	O_2	Ar	CO_2	$\mathrm{CH_4}$
McKinney	7/9/1991	14.2	3	0.531	4.8	0.00
Ruby Farms	7/9/1991	16.0	5	.612	4.3	.00
USGS 8	7/12/1991	18.4	5	.637	4.6	.00
USGS 26	7/11/1991	16.7	5	.582	4.8	.00
USGS 87	5/6/1991	20.9	6	.707	5.6	.00
USGS 100	7/8/1991	15.8	5	.558	3.4	.00
USGS 104	7/8/1991	17.2	6	.624	3.3	.00
USGS 117	5/6/1991	17.2	7	.675	1.5	.00
USGS 120	5/7/1991	17.3	9	.606	2.7	.00

Table 2.--Well construction and water levels at the time of sampling, Idaho National Engineering Laboratory, Idaho

[Elevations are in meters above sea level; depths are in meters below land surface. BLS, below land surface; --, no data; ~, approximately]

		Total	Water	Pump	Comments and
Well name	Elevation	depth	level	depth	screened interval BLS
Arco City Park 2	~1622		~42	76	Not known
McKinney	~1891	13.1	2.67		Not known
P&W2	1490.9	117.7	93.97	104	Perforated 95 to 117
Ruby Farms	~1462	198.1	~79		Open hole 170 to 198
USGS 1	1531.2	193.9	179.19	187	Perforated 183 to 192
USGS 8	1583.6	247.5	233.77	244	Perforated 238.3 to 247
USGS 9	1533.7	199.3	185.29	194	Perforated 188 to 198
USGS 18	1464.9	100.3	81.87	92	Perforated 91 to 98
USGS 23	1488.7	141.1	121.55	135	Perforated 125 to 131
USGS 26	1459.9	81.1	62.91	78	Perforated 71 to 81
USGS 27	1459.2	95.1	68.51	80	Perforated 72 to 79 & 91 to 94
USGS 58	1499.4	153.3	140.22	145	Open hole 66 to 152
USGS 65	1502.6	151.8	141.80	149	Open hole 139 to 150
USGS 79	~1462	214.0	~144	159	Open hole 81 to 214
USGS 86	1548.7	210.6	198.09	207	Open hole 15 to 211
USGS 87	1528.8	205.1	179.35	186	Open hole 178 to 195
USGS 88	1530.2	201.8	179.49	193	Perforated 173 to 202
USGS 89	1532.8	196.9	183.26	189	Open hole 176 to 197
USGS 97	1481.0	155.4	115.52	123	Open hole 118 to 155
USGS 100	1569.7	228.6	205.83	212	Open hole 202 to 229
USGS 104	1521.4	213.4	169.37	180	Open hole 168 to 213
USGS 117	1527.7	199.6	178.43	194	Perforated 168 to 200
USGS 119	1533.5	214.9	184.41	209	Perforated 195 to 215
USGS 120	1527.7	214.9	187.63	206	Perforated 194 to 215



Three water samples were determined to have gas-recharge temperatures in the range of 2 to 3°C. These waters are from wells in mountain valleys north and northwest of INEL. The ground waters recharged at elevations of 2,430 m (8,000 feet) or higher, indicating recharge from snowmelt at higher elevations (fig. 2).

Samples from wells 87 and 117, located at INEL, contained anomalous dissolved-gas compositions and will be discussed separately. Gas-recharge temperatures for the seven INEL samples ranged from 8 to 12°C, and averaged 9.7±1.3°C. This temperature is near the mean annual soil temperature of 9°C measured near the RWMC at a depth of 5 m (Davis and Pittman, 1990). Lower gas-recharge temperatures can be modeled for INEL by using a higher water-recharge elevation than INEL. The higher water-recharge elevation is not consistent with the hydrology at INEL (Barroclough and others, 1981) and would require ground-water traveltimes much greater than the 1.5-8 m·d·1 determined by Robertson and others, (1974). Therefore, it can be concluded that the N₂-Ar concentrations in the ground waters are in equilibrium with the soil atmosphere at the elevation of INEL.

Anomalous dissolved-gas results were obtained for wells 117 and 87. Well 117 plots outside of the boundaries of excess-air recharge-water-temperature graph, a deviation indicating that the dissolved-gas composition was modified. If the ground water was not contaminated during sampling and storage, then this sample would have contained about 0.07 mg·L-1 of Ar in solution from an unknown source. Similarly, sample data for well 87 will yield reasonable recharge-water temperature if Ar from an unknown source is assumed to have been added to the ground water. If this excess Ar is of natural radiogenic origin, then these two waters are millions of years old (Andrews and Lee, 1979). Such an old age seems unlikely; therefore, further sampling would be required to confirm the results and (or) find the source of the excess Ar.

Chlorofluorocarbon Content

The measured concentrations of CFC-11 and CFC-12 in the ground-water samples are presented in table 3. The concentrations of CFC-12 ranged from below the detection limit of less than 1 pg·kg-1 to greater than 70,000 pg·kg-1 of solution. The CFC-11 range in the samples was from below the detection limit of less than 1 to greater than 4,000 pg·kg-1 of solution. The exact concentration of CFC's in highly contaminated waters is uncertain because the analytical system used in this study was designed to measure ultratrace concentrations of CFC's. When CFC-11 or CFC-12 concentrations exceed a few thousand pg·kg-1 of solution, the signal of the electron capture detector becomes saturated and the output voltage of the detector exceeds the range of detection; the result is grossly underestimated CFC concentrations. Such conditions prevailed in the analysis of samples from several of the most highly contaminated wells (table 3).

Table 3. – Concentrations of dissolved chlorofluorocarbon – 11 and chlorofluorocarbon – 12 in ground waters from Idaho National Engineering Laboratory, Idaho [Detection limits of chlorofluorocarbons are less than 1 picogram per kilogram of solution. °C, degrees Celsius; BP, barometric pressure; mm, millimeters Hg; pg/kg, picograms per kilogram of solution; pptv, parts per trillion volume; CFC, chlorofluorocarbon]

			REC	HARGE 1		CONCEN	TRATION LUTION	Calculated At	mospheric	Mode	1
Well name	SAMP	LING		Elevation	BP	CFC-11		Partial Pressu			arge Dates
TTON HAITIC	Date	Time	(°C)	(m)	(mm)	(pg/kg)	(pg/kg)	CFC-11	CFC-12	CFC-11	CFC-12
Arco City Park 2		945	10	1622	625	268.1	115.6	112.3	211.9	1974.5	1974.5
Arco City Park 2		953	10	1622		270.7	116.9	113.4	214.4	1974.5	1974.5
Arco City Park 2		957	10	1622	625	259.3	109.5	108.6	200.7	1974.0	1974.0
Arco City Park 2		1000	10	1622	625	249.1	108.5	104.3	199.0	1974.0	1973.5
	7/9/91	1410	10	1891	605	537.1	245.7	232.4	465.3	1986.5	1988.5
	7/9/91	1412	10	1891	605	447.9	228.7	193.8	433.1	1982.5	1987.0
-	7/9/91	1426	10	1891	605	548.0	250.3	237.1	474.0	1987.0	1989.0
-	7/9/91	1419	10	1891	605	490.8	228.6	212.3	433.0	1984.5	1987.0
•	7/9/91	1422	10	1891	605	548.6	248.2	237.4	470.1	1987.0	1989.0
P&W2	7/11/91	1104	10	1491	635	573.0	228.7	236.2	412.7	1987.0	1986.0
P&W2	7/11/91	1102	10	1491	635	547.1	227.1	225.6	409.8	1986.0	1986.0
P&W2	7/11/91	1113	10	1491	635	610.6	235.6	251.8	425.1	1988.0	1986.5
P&W2	7/11/91	1115	10	1491	635	579.2	224.0	238.8	404.3	1987.0	1985.5
P&W2	7/11/91	1120	10	1491	635	563.6	230.7	232.4	416.4	1986.5	1986.0
Ruby Farms	7/9/91	1220	10	1492	635	48.8	24.1	20.1	43.6	1963.5	1961.5
Ruby Farms	7/9/91	1222	10	1492	635	67.3	31.1	27.7	56.1	1965.0	1963.5
Ruby Farms	7/9/91	1230	10	1492	635	44.0	18.7	18.1	33.8	1963.0	1 95 9.5
Ruby Farms	7/9/91	1232	10	1492	635	61.6	29.7	25.4	53.6	1964.5	1963.0
Ruby Farms	7/9/91	1234	10	1492	635	65.4	30.3	27.0	54.7	1965.0	1963.5
USGS 1	7/8/91	1319	10	1531	632	63.5	36.9	26.3	66.8	1964.5	1964.5
USGS 1	7/8/91	1323	10	1531	632	65.0	32.7	26.9	59.4	1965.0	1964.0
	7/8/91	1326	10	1531	632	63.8	33.4	26.4	60.6	1965.0	1964.5
USGS 1	7/8/91	1330	10	1531	632	60.0	29.2	24.9	53.0	1964.5	1963.0
	7/8/91	1335	10	1531	632	61.4	32.8	25.4	59.4	1964.5	1964.0
	7/12/91	1446	10	1584	628	57.1	63.4	23.8	115.7	1964.0	1969.0
	7/12/91	1454	10	1584	628	63.3	63.8	26.4	116.4	1964.5	1969.0
	7/12/91	1503	10	1584	628	65.5	71.5	27.3	130.4	1965.0	1970.0
	7/12/91	1203	10	1534	632	325.8	210.8	135.0	382.4	1976.0	1984.5
	7/12/91	1207	10	1534	632	330.6	186.1	137.0	337.6	1976.5	1981.5
	7/12/91	1211	10	1534	632	327.0	180.7	135.5	327.8	1976.0	1981.0
	7/12/91	1217	10	1534	632	316.4	216.6	131.1	392.9	1976.0	1985.0
	7/12/91	1222	10	1534	632	322.2	182.1	133.6	330.3	1976.0	1981.5
	7/11/91	1512	10	1465	637	8.6	6.3	3.5	11.3	1954.5	1952.0
	7/11/91	1513	10	1465	637	9.5	5.2	3.9	9.4	1955.0	1951.0
	7/11/91	1518	10	1465	637	10.1	5.9	4.1	10.7	1955.5	1952.0
	7/11/91		10	1465		10.2	5.5	4.2	9.8	1955.5	1951.5
	7/11/91	1524	10	1465	637	9.0	7.1	3.7	12.7	1955.0	1953.0
	7/11/91	909	10	1489		217.1	113.8	89 .5	205.3	1972.5	1974.0
	7/11/91	915	10	1489		205.9	103.0	84.9	185.8	1972.5	1973.0
	7/11/91	918	10	1489		218.2	113.5	89.9	204.8	1973.0	1974.0
	7/11/91	921	10	1489		202.3	98.8	83.4	178.3	1972.0	1972.5
	7/11/91	924	10	1489		222.1	109.0	91.5	196.6	1973.0	1973.5
	7/11/91	928	10	1489		255.1	121.9	105.2	220.0	1974.0	1974.5
	7/11/91	933	10	1489		233.6	110.9	96.3	200.0	1973.5	1974.0
	7/11/91	936	10	1489		221.1	110.4	91.2	199.1	1973.0	1973.5
	7/11/91	1239	10	1460		57.4	26.5	23.6	47.6	1964.0	1962.5
		1249	10	1460		57.6	26.8	23.6	48.1	1964.0	1962.5
			10	1460		53 .5	24.4	22.0	43.8	1964.0	1961.5
USGS 26	7/11/91	1300	10	1460	637	53.7	25.0	22.0	45.0	1964.0	1962.0

Table 3.——Concentrations of dissolved chlorofluorocarbon—11 and chlorofluorocarbon—12 in ground waters from Idaho National Engineering Laboratory, Idaho.

Continued

						CONCEN	TRATION				······································
			REC	HARGE 1			UTION	Calculated A	tmospheric	Mode	el
Well name	SAMP	LING	Temp.	Elevation	BP	CFC-11		Partial Press	ure in pptv	CFC Rech	arge Dates
	Date	Time	(°C)	(m)	(mm)	(pg/kg)	(pg/kg)	CFC-11	CFC-12	CFC-11	CFC-12
USGS 27	7/11/91	1410	10	1459	637	27.6	14.9	11.3	26.8	1960.5	1958.0
USGS 27	7/11/91	1412	10	1459	637	24.1	12.9	9.9	23.1	1959.5	1957.0
USGS 27	7/11/91	1415	10	1459	637	23.1	14.3	9.5	25.7	1959.5	1957.5
USGS 27	7/11/91	1418	10	1459	637	23.3	11.8	9.6	21.2	1959.5	1956.5
USGS 27	7/11/91	1420	10	1459	637	23.7	16.5	9.8	29.6	1959.5	1958.5
USGS 58	7/9/91	1642	10	1499	634	582.7	1926.9	240.5	3480.7	[1987.0]	CNT
USGS 58	7/9/91	1645	10	1499	634	571.0	1721.1	235.7	3108.9	[1986.5]	CNT
USGS 58	7/9/91	1648	10	1499	634	568.3	1906.9	234.6	3444.5	[1986.5]	CNT
USGS 58	7/9/91	1652	10	1499	634	565.0	1695.5	233.2	3062.7	[1986.5]	CNT
USGS 58	7/9/91	1656	10	1499	634	589.9	1861.8	243.4	3363.1	[1987.5]	CNT
USGS 65	7/9/91	1742	10	1503		1349.4	24782.0	557.1	44782.9	CNT	CNT
USGS 65	7/9/91	1746	10	1503	634	1527.3	21561.7	630.6	38963.6	CNT	CNT
USGS 65	7/9/91	1750	10	1503	634	1349.1	24912.3	557.0	45018.4	CNT	CNT
USGS 65	7/9/91	1754	10	1503	634		21133.5	630,2	38189.9	CNT	CNT
USGS 65	7/9/91	1759	10	1503	634		22929.5	573.2	41435.4	CNT	CNT
USGS 79	7/9/91	1907	10	1462	637	432.3	1581.2	177.6	2843.4	[1981.0]	CNT
USGS 79	7/9/91	1912	10	1462		403.8	1342.2	165.9	2413.6	[1979.5]	CNT
USGS 79	7/9/91	1915	10	1462		407.4	1502.0	167.4	2701.0	[1979.5]	CNT
USGS 79	7/9/91	1918	10	1462		393.2	1345.6	161.6	2419.8	[1979.0]	CNT
USGS 79	7/9/91	1921	10	1462		419.6	1481.8	172.4	2664.7	[1980.0]	CNT
USGS 86	7/12/91	1338	10	1549	631	616.0	192.5	255.7	349.8	[1988.5]	[1982.5]
USGS 86	7/12/91	1341	10	1549	631	350.0	145.9	145.3	265.2	1977.0	1977.0
USGS 86	7/12/91	1344	10	1549	631	385.7	159.0	160.1	289.0	1978.5	1978.5
USGS 86	7/12/91	1349	10	1549	631	315.1	168.9	130.8	306.8	1976.0	1980.0
USGS 86	7/12/91	1352	10	1549	631	313.6	129.9	130.2	236.1	1976.0	1975.5
USGS 87	5/6/91	1410	10	1529	632	172.4	4918.6	71.4	8916.5	[1971.0]	CNT
USGS 87	5/6/91	1416	10	1529	632	75.1	4739.1	31.1	8591.1	[1965.5]	CNT
USGS 87	5/6/91	1421	10	1529	632	1358.8		562.8	132566.8	CNT	CNT
USGS 88	5/7/91	1112	10	1530		228.0	4755.4	94.5	8622.0	[1973.0]	CNT
USGS 88	5/7/91	1117	10	1530		329.2		136.4	12618.3	[1976.5]	CNT
USGS 88	5/7/91	1121	10	1530			35890.7	1021.3	65073.3	CNT	CNT
USGS 88	5/7/91	1125	10	1530		2383.4		987.4	65854.3	CNT	CNT
USGS 89	5/6/91	1504	10	1533		4.7	6303.8	1.9	11432.9	[1953.0]	CNT
USGS 89	5/6/91	1507	10	1533		5.1	7855.6	2.1	14247.4	[1953.0]	CNT
USGS 89	5/6/91	1515	10	1533		41.5		17.2	62449.6	[1962.5]	CNT
USGS 97	7/9/91	1536	10	1481		3924.9	70.1	1616.3	126.3	CNT	[1969.5]
USGS 97	7/9/91	1545	10	1481	636	3948.8	74.2	1626.2	133.8	CNT	[1970.0]
USGS 97	7/9/91	1559	10	1481		3928.4		1617.8	129.9	CNT	[1970.0]
USGS 97	7/9/91	1602	10	1481		4008.9	80.5	1650.9	145.1	CNT	[1971.0]
USGS 100	7/8/91	1519	10	1570		120.3	57.3	50.1	104.4	1968.5	1968.0
USGS 100	7/8/91 7/8/91	1523	10	1570		118.4	53.5	49.3	97.4	1968.5	1967.5
USGS 100	7/8/91	1523	10	1570		117.5	57.1	48.9	104.1	1968.5	1968.0
USGS 100	7/8/91	1529	10	1570		108.8		45.3	97.1	1968.0	1967.5
USGS 100	7/8/91	1532	10	1570		122.6		51.0	110.9	1968.5	1968.5
USGS 100	7/8/91	1132	10	1521			21342.9	76.8	38655.7	[1971.5]	CNT
USGS 104	7/8/91	1136	10	1521			21602.7	61.2	39126.2	[1971.3]	CNT
									32938.9	[1970.0]	CNT
USGS 104	7/8/91	1140	10	1521			18186.5 18074.2	41.5			
USGS 104	7/8/91	1143	10	1521	633 633			30.5	32735.5 37640.3	[1965.5] [1966.5]	CNT
USGS 104	7/8/91	1149	10	1521	033	გ კ.5	20782.2	34.5	3/040.3	[1300.5]	CNT

Table 3. – Concentrations of dissolved chlorofluorocarbon – 11 and chlorofluorocarbon – 12 in ground waters from Idaho National Engineering Laboratory, Idaho.

Continued

						CONCEN					
				HARGE 1			UTION	Calculated At	•	Mode	
Well name	SAMP			Elevation	BP	CFC-11		Partial Pressu			arge Dates
	Date	Time	(°C)	(m)	(mm)	(pg/kg)	(pg/kg)	CFC-11	CFC-12	CFC-11	CFC-12
USGS 117	5/6/91	1250	10	1528	632	0.0	0.0	0.0	0.0	< 1945	< 1940
US G S 117	5/6/91	1304	10	1528	63 2	3.2	0.0	1.3	0.0	1952.0	< 1940
USGS 117	5/6/91	1307	10	1528	632	0.0	0.0	0.0	0.0	< 1945	< 1940
USGS 117	7/11/91	1716	10	1528	632	68.7	26.6	28.4	48.1	[1965.0]	[1962.5]
USGS 117	7/11/91	1720	10	1528	632	56.7	21.2	23.5	38.5	[1964.0]	[1960.5]
USGS 117	7/11/91	1725	10	1528	632	36.7	14.6	15.2	26.5	[1962.0]	[1958.0]
USGS 117	7/11/91	1730	10	1528	632	29.0	12.0	12.0	21.8	[1960.5]	[1956.5]
USGS 117	7/11/91	1735	10	1528	632	23.3	10.4	9.7	18.8	[1959.5]	[1955.5]
USGS 117	7/11/91	1740	10	1528	632	19.4	7.6	8.0	13.8	[1958.0]	[1953.5]
USGS 117	7/11/91	1745	10	1528	632	16.8	5.7	7.0	10.3	[1957.5]	[1951.5]
USGS 117	7/11/91	1750	10	1528		15.7	5.2	6.5	9.5	[1957.0]	[1951.0]
USGS 117	7/11/91	1755	10	1528		13.8	4.3	5.7	7.7	[1956.5]	[1950.0]
USGS 117	7/11/91	1800	10	1528	632	11.7	3.7	4.9	6.7	1956.0	1949.5
USGS 117	7/11/91	1805	10	1528	632	11.5	3.6	4.8	6.4	1956.0	1949.5
USGS 117	7/11/91	1808	10	1528	632	11.4	3.1	4.7	5.6	1955.5	1949.0
USGS 117	7/11/91	1811	10	1528	632	10.7	1.8	4.4	3.2	1955.5	1947.0
USGS 117	7/11/91	1814	10	1528		10.7	1.7	4.5	3.1	1955.5	1947.0
USGS 117	7/11/91	1817	10	1528		10.9	4.3	4.5	7.8	1955.5	1950.0
USGS 117	7/11/91	1820	10	1528	632	8.2	3.3	3.4	6.0	1954.5	1949.0
USGS 117	7/11/91	1823	10	1528					3.8	1954.5	1949.0
						8.4	2.1	3.5			1947.5
USGS 117	7/11/91	1847	10	1528	632	10.1	11.2	4.2	20.3	1955.5	
USGS 117	7/11/91	1850	10	1528	632	10.3	2.6	4.3	4.8	1955.5	1948.0
USGS 117	7/11/91	1855	10	1528	632	9.3	1.8	3.8	3.2	1955.0	1947.0
USGS 119	5/6/91	1546	10	1534		37.2		15.4	103.5	[1962.0]	[1968.0]
USGS 119	5/6/91	1549	10	1534		122.7		50.9	209.5	[1969.0]	[1974.0]
USGS 119	5/6/91	1551	10	1534		105.9	189.8	43.9	344.3	[1968.0]	[1982.0]
USGS 119	5/6/91	1554	10	1534		291.7	244.8	120.9	443.9	[1975.0]	[1987.5]
USGS 120	5/7/91	1018	10	1528	632	106.7		44.2	289.3	[1968.0]	[1978.5]
USGS 120	5/7/91	1022	10	1528		213.0		88.2	402.7	[1972.5]	[1985.5]
USGS 120	5/7/91	1027	10	1528	632	481.1	484.8	199.2	878.8	[1982.5]	CNT
USGS 120	5/7/91	1034	10	1528		492.7	499.4	204.0	905.2	[1984.0]	CNT
USGS 120	7/12/91	930	10	1528	632	747.5	1117.1	309.5	2024.8	CNT	CNT
USGS 120	7/12/91	940	10	1528	632	1128.9	631.3	467.5	1144.3	CNT	CNT
USGS 120	7/12/91	945	10	1528	632	1146.3	966.0	474.7	1751.0	CNT	CNT
USGS 120	7/12/91	950	10	1528	632	909.7	1191.6	3 76.7	2159.8	CNT	CNT
USGS 120	7/12/91	955	10	1528	632	1024.0	710.3	424.1	1287.5	CNT	CNT
USGS 120	7/12/91	1000	10	1528	632	940.1	1206.4	389.3	2186.6	CNT	CNT
USGS 120	7/12/91	1005	10	1528	632	1053.3		436.2	1129 4	CNT	CNT
USGS 120	7/12/91	1010	10	1528	632	946 8	1221 3	392.1	2213.7	CNT	CNT
USGS 120	7/12/91	1015	10		632	974.5		403.6	2226.4	CNT	CNT
USGS 120	7/12/91		10	1528		958.6		397.0	3914.9	CNT	CNT
USGS 120	7/12/91	1025	10	1528		950.1	1188.2		2153.6	CNT	CNT
USGS 120	7/12/91							393.5			
			10	1528		901.8		373.4	1916.6	CNT	CNT
USGS 120	7/12/91		10	1528		959.4	1233.3	397.3	2235.5	CNT	CNT
USGS 120	7/12/91		10	1528		961.4		398.2	2217.3	CNT	CNT
USGS 120	7/12/91		10	1528		963.8		399.2	2210.7	CNT	CNT
USGS 120	7/12/91		10	1528		974.5		403.6	2210.3	CNT	CNT
USGS 120	7/12/91		10		632	964.5		399.5	2261.4	CNT	CNT
USGS 120	7/12/91		10		632	951.6		394.1 Idel CEC age of	2458.7	CNT	CNT

¹ The recharge temperature and barometric pressure used influence the model CFC age obtained. A higher temperature will also yield younger CFC – 11 and CFC – 12 ages. A higher barometric pressure will yield younger CFC – 11 and CFC – 12 ages.

² The prefix < designation in < 1945 indicates model CFC-11 or CFC-12 dates earlier than 1945.

The square brackets in [1985] indicate suspected contamination with CFC-11 or CFC-12. The age of the sample may be older than the apparent 1985 age in the square brackets.

The abbreviation CNT indicates that the sample cannot be dated. The calculated CFC-11 or CFC-12 partial pressures are greater than the CFC-11 or CFC-12 concentrations in the 1991 atmosphere.

³ The CFC-model recharge dates were calculated on the basis of well elevations.

AGE DATING GROUND WATERS BY THE USE OF CHLOROFLUOROCARBONS

The age of ground water, as implied by the CFC method, is defined as the time since the water became isolated from the unsaturated-zone atmosphere. To a first approximation, the ground-water age refers to the time of ground-water recharge. Uncertainties result from the many assumptions and complications involved in interpreting ground-water age from the CFC concentration in the water. Because of these uncertainties, CFC ages of ground water are referred to as CFC-model recharge ages. Valid CFC-model recharge ages can be obtained only if the aquifer is not contaminated by local sources of CFC's, the water sample analyzed is not contaminated during collection, the water sample contains CFC concentrations that are representative of the amounts present in the aquifer, and the CFC concentrations in the aquifer were not modified by geochemical, biological or hydrologic processes after entering the saturated zone (Busenberg and Plummer, 1992; Plummer and others, 1993). CFC age dating may not be possible in some urban areas (Appleby, 1976; Hester and others, 1974; Frank and others, 1991) where atmospheric CFC concentrations are significantly greater than in non-urban areas. The CFC model recharge ages should be regarded as minimum estimates of age because of the possibilities of contamination of the ground water with CFC's or chance introduction of CFC's into the samples during the sampling process. CFC-model recharge ages are more uncertain for older waters than for younger waters because older waters contain lower CFC concentrations and are more sensitive to trace contamination.

The atmospheric partial pressures of CFC-11 and CFC-12 are calculated from their concentrations in the ground water through Henry's law (eq 1). The calculated partial pressures are compared to the atmospheric growth curves to obtain the age of the ground water (Busenberg and Plummer, 1992).

Reconstruction of the Chlorofluorocarbon Concentrations in the Atmosphere

The concentrations of CFC-11 and CFC-12 in the atmosphere have been rapidly increasing since the industrial introduction of CFC's in the late 1930's. No atmospheric measurements of CFC's are available before 1970. McCarthy and others, (1977) describe the procedures used to estimate the atmospheric inventory of CFC-11 and CFC-12 from the production records compiled by the Chemical Manufacturers Association (AFEAS, 1992). The historical global atmospheric inventory is then normalized to measured atmospheric concentrations at a particular location to obtain the pre-1977 atmospheric concentrations (McCarthy and others, 1977; Gamlen and others, 1986; Busenberg and Plummer, 1992). In this study, the pre-1975 atmospheric release

Table 4.--Yearly average concentrations of chlorofluorocarbon-11 and chlorofluorocarbon-12 in the atmosphere¹
[Concentrations units are parts per trillion volume per volume]

Year	CFC-11	CFC-12	Year	CFC-11	CFC-12	Year	CFC-11	CFC-12
1940.0	0.012	0.332	1957.5	6.85	24.35	1975.0	115.3	220.4
1940.5	.014	.394	1958.0	7.51	26.07	1975.5	122.9	230.6
1941.0	.016	.474	1958.5	8.16	27.80	1976.0	129.8	240.3
1941.5	.019	.554	1959.0	8.82	29.73	1976.5	136.0	249.9
1942.0	.021	.653	1959.5	9.48	31.66	1977.0	143.0	259.0
1942.5	.023	.752	1960.0	10.36	33.96	1977.5	147.7	268.1
1943.0	.028	.872	1960.5	11.24	36.26	1978.0	150.9	277.9
1943.5	.032	.992	1961.0	12.37	38.84	1978.5	157.5	288.1
1944.0	.037	1.160	1961.5	13.51	41.41	1979.0	160.8	293.3
1944.5	.041	1.320	1962.0	14.95	44.37	1979.5	163.7	296.3
1945.0	.048	1.530	1962.5	16.38	47.32	1980.0	169.7	306.2
1945.5	.055	1.750	1963.0	18.14	50.78	1980.5	173.9	312.3
1946.0	.069	2.120	1963.5	19.89	54.24	1981.0	177.1	317.5
1946.5	.082	2.490	1964.0	21.98	58.27	1981.5	180.9	328.4
1947.0	.113	3.060	1964.5	24.06	62.29	1982.0	185.0	338.1
1947.5	.143	3.640	1965.0	26.42	66.82	1982.5	189.6	347.0
1948.0	.197	4.300	1965.5	28.77	71.36	1983.0	194.5	355.8
1948.5	.251	4.960	1966.0	31.40	76.39	1983.5	199.3	366.2
1949.0	.339	5.670	1966.5	34.02	81.42	1984.0	203.2	372.5
1949.5	.428	6.380	1967.0	36.98	87.09	1984.5	207.4	380.0
1950.0	.556	7.160	1967.5	39.95	92.76	1985.0	212.6	389.0
1950.5	.684	7.940	1968.0	43.31	99.11	1985.5	218.7	396.8
1951.0	.859	8.790	1968.5	46.67	105.50	1986.0	224.4	407.9
1951.5	1.040	9.640	1969.0	50.57	112.50	1986.5	229.4	416.6
1952.0	1.290	10.520	1969.5	54.47	119.60	1987.0	235.0	426.6
1952.5	1.540	11.410	1970.0	58.89	127.30	1987.5	242.6	442.1
1953.0	1.890	12.390	1970.5	63.30	135.00	1988.0	250.3	452.1
1953.5	2.230	13.380	1971.0	68.11	143.20	1988.5	255.6	461.5
1954.0	2.660	14.500	1971.5	72.93	151.40	1989.0	259.1	469.0
1954.5	3.080	15.620	1972.0	78.34	160.30	1989.5	263.7	476.2
1955.0	3.600	16.870	1972.5	83.75	169.20	1990.0	267.6	485.0
1955.5	4.120	18.120	1973.0	89.93	179.10	1990.5	269.0	491.5
1956.0	4.770	19.580	1973.5	96.11	189.00	1991.0	270.6	495.6
1956.5	5.410	21.040	1974.0	102.90	199.60	1991.5	272.8	501.1
1957.0	6.130	22.690	1974.5	109.60	210.30	1992.0	274.6	510.5

¹ 1940-76 CFC concentrations were modeled from production and release data of the Chemical Manufacturers Association (McCarthy and others, 1977). 1977-1992 data are semiannual averages of measured concentrations (Elkins and others, 1993).

Figure 3.--Concentrations of chlorofluorocarbon-11, and chlorofluorocarbon-12 in the atmosphere.

data were normalized to measured concentrations at Niwot Ridge, Colo. (Elkins, 1993). The pre-1977 CFC growth curves (fig. 3) are nearly identical to other published curves (Bullister, 1984; Wisegarver and Gammon, 1988; Smethie and others, 1988). The post-1977 atmospheric concentrations of CFC-12 and CFC-11 for Idaho (table 4 and fig. 3) are believed to be the same as the concentrations measured at Niwot Ridge, near Boulder Colo. (Elkins, 1993).

Chlorofluorocarbon-Model Ages of Recharge

Model CFC-age calculations are based on the assumption that CFC-11 and CFC-12 concentrations in the recharge water are proportional to the tropospheric concentrations at any particular time and location. This hypothesis implies that (1) the CFC concentrations in the recharge waters are in equilibrium with the soil atmosphere and (2) CFC concentrations in the soil and troposphere are nearly identical. These assumptions are reasonable where the unsaturated zone is thin and recharge occurs by slow infiltration through the unsaturated zone. For example, a concentration difference observed between the unsaturated-zone atmosphere at 3 m depth and air for CFC-11 and CFC-12 was small at INEL. This concentration difference will cause an uncertainty of about 1 year or less in the calculated CFC-11 and CFC-12 ages of the waters. When recharge occurs through a thin unsaturated zone, the calculated recharge-water temperature from the dissolved gases was found to be the same as the mean annual air and soil temperatures at the water table (Heaton, 1981; Heaton and Vogel, 1981; Andrews and others, 1985; Mazor, 1972; Herzberg and Mazor, 1979; Andrews and Lee, 1979). If recharge occurs by slow percolation through a very thick unsaturated zone (Weeks and others, 1982), CFC age dating may not be possible.

In general, the results of sampling soil gases for CFC's indicates that the data can be explained by gaseous diffusion through an immobile reservoir (Weeks and others, 1982). Because the diffusive transport of CFC-11 is slower than that of CFC-12, the apparent CFC-11 age of recharged water having a long residence time in the unsaturated zone will be significantly greater than its apparent age based on CFC-12. For example, at a depth of 58 m at TAN, the measured apparent CFC-11 and CFC-12 ages of the unsaturated-zone atmosphere was 28.5 and 21.0 years, respectively. At some other locations, the unsaturated zone is more than 275 m thick, and water in equilibrium with the soil atmosphere at the water table should give older apparent CFC-model ages. In addition, at the depth of 275 m, the differences between the CFC-11 and the CFC-12 ages should be greater than what was observed at the depth of 58 m.

In 83 percent of the uncontaminated deep wells, the CFC-11 and CFC-12 ages agree to within ± 2 year; in the remaining 17 percent of the wells, the calculated CFC-11 and CFC-12 ages agree to within ± 4 years. These results are consistent with the equilibration of ground waters near or within the thin-soil zone without any further reequilibration with the unsatu-

rated-zone atmosphere in the fractured basalts near the water table. Flow through fractures in the unsaturated zone may inhibit gas-water equilibration because of limited contact between water and unsaturated-zone gas. In addition, the rapid recharge that occurs during flooding reduces the time the water is in contact with the deep unsaturated-zone atmosphere and may help preserve the shallow dissolved-gas composition of the water. This model of recharge is consistent with (1) CFC concentrations in the water, (2) the temperature obtained from gas solubilities of Ar and N_2 , and (3) water level measurements after flooding or flow of the Big Lost River through INEL (Bennett, 1990; Barraclough and others, 1981). In only one deep well (USGS 8), the calculated CFC-11 age is more than 2 years greater than the CFC-12 age, consistent with the hypothesis of slow percolation through a very thick unsaturated zone and gas-water equilibration at the water table.

Uncertainties in Chlorofluorocarbon-Model Recharge Ages

Because the concentrations of CFC's and other gases in ground water depend on atmospheric partial pressures and temperature, the equilibration temperature during recharge must be known for age dating. In areas where unsaturated zones are thick, the recharge-water temperature is similar to the mean annual air and (or) soil temperature (Mazor, 1972; Herzberg and Mazor, 1979; Heaton and Vogel, 1981; Andrews and Lee, 1979). In mountainous areas, the recharge elevation and recharge-water temperature may be difficult to evaluate. A 1°C uncertainty in the calculated N_2 -Ar recharge-water temperature results for every 210 m uncertainty in the recharge elevation.

Table 5 gives the errors introduced in the model CFC-11 and CFC-12 ages when the recharge-water temperature is overestimated or underestimated by 1 to 3°C for a recharge-water temperature of 10°C. Column 1 of table 5 gives the number of years of error introduced in the model CFC-11 (column 2) and CFC-12 (column 3) dates. Columns 2 and 3 give the dates affected by 1- to 3°C-errors in the recharge-water temperature. The corrections that has to be subtracted or added to the CFC-11 and CFC-12 model dates are given on the same row in column 1. The errors introduced in CFC-dating are large for waters that recharged at low temperatures, and for young ground waters. For example, an uncertainty of ± 2 °C introduces an error in the CFC-11 and CFC-12 ages that is 1 year or less for waters older than 14 years but is 3 years for waters that are 1 year old. Dissolved N₂-Ar solubilities can be used to evaluate recharge-water temperatures to within 2°C if the recharge elevations are known.

Errors resulting from use of incorrect elevations have been evaluated and are shown in table 6. The first column of this table gives the number of years that have to be added for an underestimation of the recharge elevation for CFC-11 (column 2) and CFC-12 (column 3) dates.

Table 5.--Effects of recharge temperature on the model chlorofluorocarbon dates [Corrections were calculated at 1-degree intervals for recharge at 10 degrees Celsius. °C, degree Celsius; ---, not applicable]

		Tempera	ature of Recl	arge Overestimated					
Correction, number		CFC-11			CFC-12				
of years1	1°C	2°C	3°C	1°C	2°C	3°C			
0	1945-78	1945-75	1945-66	1940-78	1940-74	1940-56			
1	1977-88	1976-77	1967-75	1979-90	1975-78	1957-76			
2	1989-91	1978-87	1976-78	1991	1979-87	1977-81			
3		1988-91	1979-86		1988-91	1982-87			
4			1987-88			1988-90			
5			1989-91			1991			

Temperature of Recharge Underestimated

Correction, number		CFC-11			CFC-12			
of years 2	1°C	2°C	3°C	1°C	2°C	3°C		
0	1945-74	1945-57	1945-53	1940-74	1940-51	1940-48		
1	1975-89	1958-77	1954-75	1975-90	1952-78	1949-75		
2	1990-91	1978-89	1976-78	1991	1979-89	1976-79		
3		1990-91	1979-82		1990-91	1980-90		
4			1983-90			1991		
5			1991					

¹ Subtract correction from model CFC dates to correct for recharge at lower temperatures.

Columns 2 and 3 are subdivided into three secondary columns each, representing the effects of 305, 610, and 914 m in elevation. In each secondary column are shown the dates that are affected by the various elevation errors; these dates correspond to the correction in years given on the same row in column 1. For example, an underestimation of the recharge elevation by 914 m will increase 1979-87 CFC-11-model dates and 1978-87 CFC-12-model dates by 2 years. The error in the CFC ages resulting from underestimation or overestimation of recharge elevations is small for waters 10 or more years old but can be considerable for younger ground waters. These corrections are independent of the recharge temperature of the water.

² Add correction to model CFC dates to correct for recharge at higher temperatures.

Table 6.--The effects of recharge elevation on the model chlorofluorocarbon dates

[Age corrections were calculated for 305, 610, and 914 meters. Elevation effects are independent of recharge temperature. m, meter; ---, not applicable]

Correction,	****	CFC-11			CFC-12	
number of	305 m	610 m	914 m	305 m	610 m	914 m
years ¹	(1000 feet)	$(2000 \; \text{feet})$	(3000 feet)	(1000 feet)	$(2000 \; feet)$	(3000 feet)
0	1945-87	1945-76	1945-75	1940-88	1940-77	1940-72
1	1988-89	1977-87	1976-78	1989-91	1978-87	1973-77
2	1990-91	1988	1979-87		1988-91	1978-87
3		1989-91	1988-91			1988-91

¹ Add correction to model CFC-dates to correct for recharge at higher elevations.

The model CFC recharge ages of young waters (less than 10 years old) can be in error by several years if incorrect recharge temperatures (table 5) and recharge elevations (table 6) are used in calculating the CFC ages. For example, the McKinney well, located near Birch Creek about 8 km north of the INEL boundary, gave a CFC-model recharge date of 1979 and 1981 with CFC-11 and CFC-12, respectively, based on a 5°C temperature and an elevation of 2,286 m (7,500 feet). The measured N₂-Ar recharge temperature, 10°C, indicates that the recharge occurred locally at 1,890 m (6,200 feet) and not at higher elevations. The CFC-model recharge dates based on the lower elevation and higher recharge temperature are 1986 and 1988 with CFC-11 and CFC-12, respectively. This calculation demonstrates the importance of using the best available information in modeling CFC ages of young ground waters.

Changes in recharge temperature (table 5) and elevation (table 6) do not significantly affect the CFC-model recharge ages of waters older than 20 years. An error of as much as 914 m (3,000 feet) in the recharge elevation will change the CFC-model recharge age by 1 year or less. The age of water from the Arco City Park 2 well was recomputed on the basis of the well elevation and a 5°C recharge temperature. The CFC-model recharge ages increased from 18 to 19 years. It can be concluded that the CFC ages of representative INEL waters can be refined with additional dissolved-gas sampling but that the ages will not substantially change.

Some of the regional ground water may be older than the age implied by the CFC-model recharge ages near the southern boundary of INEL. Well 117 was sampled twice; in the May 1991 sampling, CFC's were completely absent in most of the samples. Therefore the recharge of the ground water preceded the introduction of CFC's. An age greater than 50 and greater than 45 years must be assigned because of absence of CFC-12 and CFC-11, respectively.

Well 117 was resampled at approximately 5-minute intervals during a 2-hour purge test in July 1991. Six borehole volumes were discharged during this test. After three borehole volumes, the CFC-11 and CFC-12 concentrations in the water stabilized (table 3). From the CFC-11 and CFC-12 concentrations, CFC-model recharge ages of 36 and 43 years were calculated. The main procedural difference between the May and July sampling was the rate of purging, which was two times faster in July. The nonconcordant CFC-11 and CFC-12 ages indicate that the July samples were mixtures of predominantly old CFC-free water with younger water. Similar results were obtained for well 120, where lower concentrations of CFC's were found in the May sampling (table 3). The well was purged at 75.7 L·min-1 during both sampling periods; however, the well was pumped for a longer time in July (99 min) than in May (59 min). The drawdown during the July sampling may have introduced shallower, younger water and may have been responsible for the observed differences in CFC concentrations.

In some wells, the concentrations of CFC's increased with time and the CFC-model recharge ages became progressively younger (wells 88, 89, 119, and 120, May sampling). In some wells near the RWMC, the CFC concentrations increased from normal background to contaminant levels during the course of sampling (table 3). These results are important because they show that (1) the rate and duration of well purging can significantly affect the concentrations of trace organics in contaminated wells and (2) the ground water is stratified with the younger or contaminated water near the water table.

Ground waters contaminated with chlorofluorocarbons

Of the 24 wells sampled for CFC's in the Snake River Plain aquifer, 10 contained water with contaminant levels of CFC-12 and (or) CFC-11 (figs. 4 and 5). Contaminant levels are defined as concentrations that are greater than the equilibrium concentration with the 1991 atmosphere at the recharge temperature of 10°C and INEL elevation. Eight wells (wells 58, 65, 79, 87, 88, 89, 104, 119 and 120) were contaminated with CFC-12, and four of these wells were also contaminated with CFC-11 (wells 65, 87, 88 and 120). Samples from well 97, located just south of the Naval Reactors Facility, indicated contamination with CFC-11 but little or no contamination with CFC-12. All three wells sampled near the Test Reactors Area (TRA) show significant contamination with CFC-12 (fig. 5). For example, wells 79, 58 and 65 contained water with concentrations of CFC-12 that were 4, 6, and 70 times greater than the equilibrium concentration of water with the 1991 atmosphere. Samples from four wells sampled around the Radioactive Waste Management Complex (RWMC) also indicated significant contamination with CFC-12 (from 4 to more than 100 times greater than the equilibrium concentration with the 1991 atmosphere). Well 104 is the only other well yielding samples that indicated significant contamination with CFC-12 (about 65 times greater than the equilibrium concentration with the 1991 atmosphere). This well is approximately 11 km south of the TRA and 8 km east of RWMC. Mann (1990) and Mann and Knobel (1987) have also reported concentrations of CFC-12 greater than 200,000 pg·L-1 in wells 88, 89, 90, 112, 113, and EBR 1 in samples collected from 1987 through 1989.

These results indicate the possibility of a large CFC-12 waste plume at INEL. The plume seems to originate near TRA or possibly ICPP and may extend to the southwest to RWMC. The farthest western extension of the CFC-12 plume was observed at well 9. This observation was based on the CFC-model recharge ages of well 9. The CFC-11 ages all four samples collected were calculated to be 15 years. The CFC-12 ages were less and ranged from 6.5-10 years; the discrepancy indicates that the water at well 9 may be slightly contaminated with CFC-12.

A secondary source of CFC-12 to this plume may be the RWMC, where an estimated 335,000 L of organic wastes was buried before 1970, including about 92,000 L of carbon tetrachloride; 148,000 L of used lubricating oil; and 95,000 L of other organic compounds, including trichloroethane, trichloroethylene, perchloroethylene, toluene, and benzene (Mann and Knobel, 1987). In fact, high concentrations of most of these organic compounds, CFC-11, and CFC-12 are present in water from well 92 (Mann, 1990). This well, which was completed above the 73-m sedimentary layer, samples the perched water table below the RWMC (Barraclough and others, 1976).

In well 104, the CFC-11 concentration varied significantly (74-186 pg·kg-1 of solution), which may indicate that the CFC-11 concentration was also modified by contamination. If the CFC-11 concentration was modified, then the water is older than the calculated CFC-11 model recharge age of 20 to 26 years. If a 20-year age is assumed from the CFC-11 data, the CFC-12 concentration is 200 times greater than its equilibrium concentration with the 1971 atmosphere. Thus, the well is heavily contaminated with CFC-12, and the contamination plume may extend a few kilometers further to the southeast from well 104. A mapped tritium plume in 1988 (Orr and Cecil, 1991; Mann and Cecil, 1990) extended only slightly beyond well 104. This difference in the extent of the plumes may result from an approximate tenfold decay in tritium activity at the leading edge of the tritium plume since the first disposal of tritium in 1952. Mann and Cecil (1990, figs. 9 and 10) reported a shrinking of the tritium plume between 1985 and 1988. Alternatively, the two tracers may have been introduced into the aquifer from different locations, or the CFC-12 may have been added to the aquifer earlier than the tritium contamination. The CFC-12 plume closely resembles the model-projected chloride plume of Robertson (1974, fig. 17), indicating that CFC-12 plume originated at TRA and ICPP.

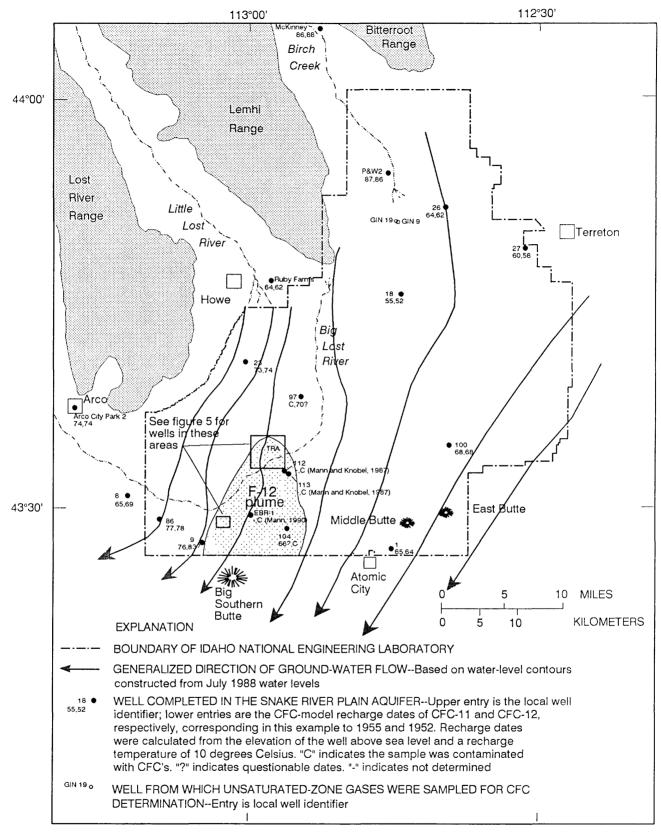


Figure 4.--Locations of selected wells and model chlorofluorocarbon-11 and chlorofluorocarbon-12 recharge dates, Idaho National Engineering Laboratory and vicinity.

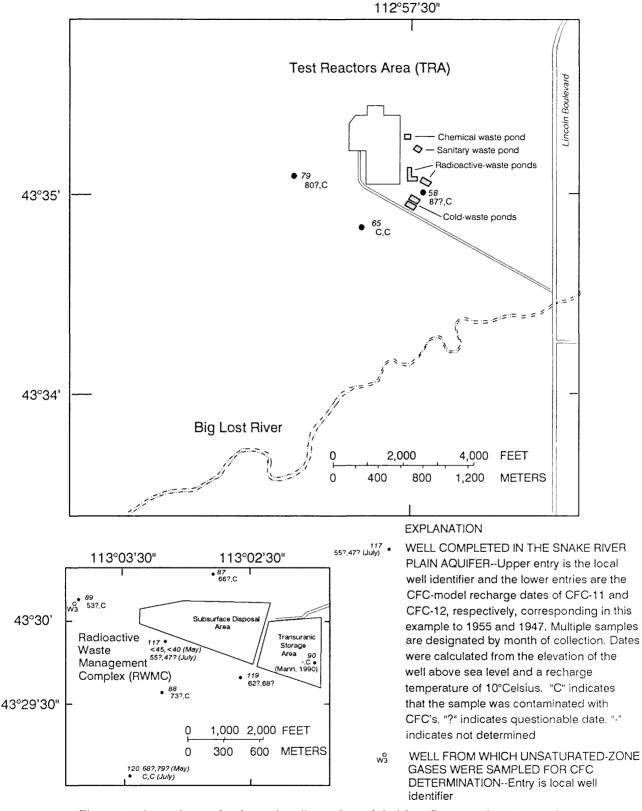


Figure 5.--Locations of selected wells and model chlorofluorocarbon-11 and chlorofluorocarbon-12 recharge dates, Test Reactors Area and Radioactive Waste Management Complex.

The CFC-12 contamination plume may also extend beyond the tritium plume to the southwest and west of RWMC beyond wells 89 and 120, which are heavily contaminated, to well 9, which may be slightly contaminated. If it is assumed that well 9 is at the leading edge of a contamination plume originating at TRA in 1952, the indicated travel time is about 1.2 m·d·l. The velocity is reasonable and consistent with the velocities of flow of 1.5 to 8 m·d·l reported by Robertson and others (1974) for the Snake River Plain aquifer. The velocity of flow reported here is, however, uncertain for three reasons, (1) the source of the CFC-12 contamination may not have been TRA but may have been the nearby RWMC, (2) the 1952 date used in this calculation is the earliest known date of discharge of wastes at TRA (the CFC-12 contamination of the ground water may have started at a much later date), and (3) the farthest extent of the CFC-12 waste plume has not been determined at this time. More extensive sampling of the ground waters for CFC's may pinpoint the source and determine the size of the CFC-12 waste plume. From such information, a improved estimate of the flow velocities could be made.

Age of Recharge at the Idaho National Engineering Laboratory

Water levels at the time of sampling and well-construction information are listed in table 2, and the concentrations of CFC-11 and CFC-12 in solution are shown in table 3. The calculated ages from CFC concentration range from 4 to greater than 50 years. Most of the waters have CFC-model ages of between 14 and 30 years (table 3). The 4-year old water was sampled near a known local recharge area. All ages have been calculated from the date of sampling, the year 1991.

The age of recharged ground water can be used in conjunction with hydrologic data to identify sources of recharge, to estimate ground-water traveltimes, and to elucidate ground-water recharge mechanisms. These applications are illustrated by sampling results from various wells, based on their proximity to sources of recharge. Previous studies (Barraclough and others, 1981, for example) indicate that these sources are infiltration from the streambeds and discharge playas of Big Lost River, Little Lost River, and Birch Creek. In addition, recharge occurs from infiltration of streamflow and applied irrigation water in the Mud Lake-Terreton area.

Many of the wells sampled are near the Big Lost River and should show effects of recharge from that source. In particular, Arco City Park 2, wells 8, 9, 86, 87, 89, 97, 104, 117, 119, and 120 are all near its channel. Some of these wells are contaminated, but waters from six wells, Arco City Park 2, 8, 9, 86, 97, and 104, all have CFC-11-based ages ranging from 14 to 27 years; at three wells (Arco City Park 2, 9, and 86) age of the water is a remarkably consistent 14 to 17 years. The mid-1970's age for Arco City Park 2, wells 9, and 86 are consistent with high streamflows in the Big Lost River as far downstream as TRA in 1974, 1975, and 1976 and little flow for several years thereafter (Barraclough, Lewis and others, 1981). Possibly, the water

recharged from the channel (Bennett, 1990) at that time has moved to its current position nearly parallel to the channel by subsequent recharge events. Ground-water traveltimes for these three wells are about 0.5-0.7 m·d·1. Well 8 is about as near the Big Lost River channel as Arco City Park 2, 9, and 86 are, but samples from well 8 have a somewhat older model age of 22-27 years. This discrepancy may be explained in part by well construction; well 8 is cased to a depth of 5 m below the water table, whereas the deepest casing for the other wells is only 3 m below the water table. Hence, the samples from well 8 may represent a mixture of old and recently recharged ground water.

Two wells presumably affected by recharge from the Little Lost River were sampled, Ruby Farms and well 23. The Ruby Farms well, however, contains relatively old water compared to other wells near the river channels. The Ruby Farms well is cased 91 m below the water table (table 2). Perhaps this well sampled water that recharged from the Little Lost River a considerable distance upstream from the well. Well 23, which is cased to a depth of 4 m below the water table, contains water of a typical 17-19 year age. Ground-water traveltime from the Little Lost River near Howe to well 23 is indicated to be about 1.5 m·d·1.

The youngest waters sampled were from two wells near Birch Creek, the McKinney well and the P&W2 well. Waters from both wells have CFC-model ages of a few years and a recharge temperature of 9°C, indicating local recharge from Birch Creek. Two other wells that are also probably affected by recharge from Birch Creek, wells 18 and 26, were sampled. These wells are located some distance from the Birch Creek Playa, and they contain waters having CFC-model ages of about 38 and about 28 years, respectively. Well 18 seems to be on a direct flow path from the playa, and, assuming no downgradient recharge, the age implies a ground-water velocity of about 0.9 m·d·1. Water levels in well 18 respond to recharge from Big Lost River (Barraclough and others, 1981, fig. 15), but the regional water-table gradient and the relatively old model ages for the well indicate that the water moving past the well is derived from recharge along Birch Creek.

Three wells that should be on a flow path from recharge in the Mud Lake-Terreton area also were sampled. Water from well 27, nearest Terreton, has an approximate CFC-model age of 33 years. Well 27, however, is perforated through two intervals, and the samples from that well may represent a composite of deeper old water and shallow younger water. The other two wells, well 1 and well 100, yield calculated ages of 26-27 and 23 years, respectively. The integrated ground-water velocity from the presumed recharge area is about 5 m·d·1. Furthermore, if it is assumed that well 1 is on the same flow path as well 100, the indicated traveltime is on the order of 10 m·d·1. These velocities are at the high end of the range of velocities of 1.5-8 m·d·1 determined by Robertson and others, (1974).

The CFC results show that young ground water was added at various locations to the older regional ground water (more than 50 years) within and outside the INEL boundaries. The wells drilled into the Snake River Plain aquifer sampled mainly this local recharge, resulting in the complex age pattern shown in figure 4. (Average ages were plotted for all wells that are believed not to have been contaminated with CFC's; however, the oldest calculated ages are shown for wells suspected to be contaminated with CFC's. Contamination decreases the apparent CFC age of ground waters.) The Big Lost River, Birch Creek, the Little Lost River, and the Mud Lake area are major sources of recharge to the Snake River Plain aquifer at INEL. Further studies would need to be conducted to determine spatial variations in ground-water age as a function of depth. The CFC-model ages also could be used with regional flow models to improve definition of the regional flow system in the Snake River Plain aquifer at INEL.

DISTRIBUTION OF CHLOROFLUOROCARBONS IN THE UNSATURATED ZONE

CFC concentrations in the unsaturated-zone gases were measured at two different areas, at seven depths in well W³ near the RWMC and in five wells at the Test Area North (TAN) in July 1991 (figs. 1 and 4). The measured CFC concentrations are given in table 7. The results obtained at these two locations differ substantially and will be discussed separately.

Radioactive Waste Management Complex

Chloromethane concentrations were measured in air samples collected from seven different piezometers that were previously installed at depths of 73.2, 54.9, 41.1, 34.1, 22.6, 14.6, 4.6 m in well W^3 . Well W^3 is less than 600 m west of the Subsurface Disposal Area of the RWMC (fig. 5). One to three samples were taken from each piezometer, as well as a surface air sample and a N_2 blank.

Very high CFC concentrations were present in the gas samples collected from all seven piezometers. For example, the measured concentrations for CFC-11 and CFC-12 from the 4.6-m piezometer were 6,600 and 19,100 pptv (10^{-12} volume per volume, parts per trillion volume per volume), respectively. These values are 21 and 37 times greater than the CFC-11 and CFC-12 concentrations in the air sample collected at this site, respectively. The data imply the possibility of a significant flux of CFC's from the unsaturated zone into the atmosphere near well W³. The air sample collected at this site had higher concentrations of CFC-11 and CFC-12 (11 and 1 percent, respectively) than the mean 1991 air concentrations, a result that seems to confirm the above conclusion; however, further sampling near the RWMC would be required to evaluate the areal extent of the near-surface CFC anomaly and to accurately determine the fluxes of halo-

carbons into the atmosphere. The required samples could be easily obtained from air piezometers installed in shallow test holes. Alternatively, the flux of CFC's into the atmosphere could be measured by use of the simple apparatus developed by Khalil and Rasmussen (1989).

Table 7.--Concentrations of chlorofluorocarbon-11 and chlorofluorocarbon-12 in the unsaturated zone at Idaho National Engineering Laboratory, Idaho
[CFC concentrations are in parts per trillion volume per volume; depth is in meters below land surface; --, no data or not applicable]

		1991		1979		
Sample	Depth _	CFC-11	CFC-12	CFC-11	CFC-12	
$\overline{\mathbf{W}^3}$	4.6	6,600	19,100			
W^3	14.6	7,770	20,800			
W^3	22.6	10,000	22,900			
W_3	34.1	9,820	23,500			
W^3	41.1	13,700	33,200			
W^3	54.9	11,700	29,400			
W_3	73.2	10,700	34,300			
Blank		1	0			
Air		313	508			
GIN-19	3.0	279	492	(1)	(1)	
GIN-19	31.7	116	269	58	126	
GIN-19	41.1	80	207	38	130	
GIN-19	57.6	19	137	6	150	
Blank		0	0			
Air		273	498	164^{2}	296^2	
GIN-9	3.0	275	492	136	207	
GIN-9	16.5	131	305	58	124	
GIN-9	24.4	157	274	50	96	
Blank		0	0		- -	
Air		273	498	164^2	296^2	

¹ Concentration not measured.

² Assumed CFC-11 and CFC-12 concentrations in 1979 atmosphere (table 4).

The highest CFC-11 concentration in well W³ was measured at 41.1 m, and the concentrations were lower above and below this sampling point (table 7). As for CFC-12, the highest value was measured at a depth of 73.2 m, whereas the second highest concentration was observed at 41.1 m. Concentrations of CFC-12 decreased above the depth of 41.1 m. The CFC-concentration profiles (table 7) appear to have been highly influenced by the stratigraphic sequence at W³-well site. The highest halocarbon concentrations were found between the 73-m deep and 34-m deep sedimentary interbeds in the basalt sequence (Barraclough and others, 1976).

Mann and Knobel (1987) reported contaminant levels of CFC-11 and CFC-12 in well 92 which is one km due east of well W3 and which samples the perched-water table just above the 73-m-deep sedimentary interbed below the RWMC. All the above evidence indicates that the most likely source of CFC contamination may be the RWMC and that the sedimentary interbeds may have influenced the lateral transport of CFC's in the unsaturated zone. The observed CFC profiles are difficult to explain, however water percolating through the waste-burial ground might have picked up CFC contamination, migrated downward to one or both the 34-m-deep and 73-m-deep sedimentary interflow beds, and then became temporarily perched. The perched water could have then migrated downdip. However, the sedimentary beds dip to the east, away from well W3. Alternatively, the pattern might be explained as CFCs originating from a surface source that were leached by infiltrating water and transported downward. Any surface source seems improbable, as do percolation rates rapid enough to create contamination to the observed depths. If the source of the CFC's was from the underlying ground water, one would expect a fairly uniform concentration gradient decreasing upward to provide a diffusion gradient for CFC transport. The observed profiles are complex and difficult to explain by any of the above hypotheses.

Test Area North

Chlorofluorocarbons from various depths in the unsaturated zone were sampled in 1979 and again in 1991 at a piezometer installation near TAN (fig. 1). The samples were collected from two piezometer nests (GIN 9 and GIN 19; Schmalz, 1969) that tap the sediments of Birch Creek playa and the underlying Snake River Plain basalts. The two nests, which were chosen from a total of 14 that had been installed, were selected on the basis of their use in a previous air-permeability test (Weeks, 1978). At both nests, the playa sediments overlying the basalts are about 16 m thick, and the unsaturated basalts extend to the water table at a depth of about 46 m. The nest at GIN 9 includes three piezometers in separate adjacent boreholes. One piezometer extends to a depth of 24.4 m, thus penetrating about 8 m of basalt. Another extends to the playa sediment-basalt contact at a depth of 16.5 m and the third to a depth of 3 m in playa

sediments. GIN 19 includes three piezometers in a single hole, all tapping basalt, at depths of 31.7, 41.1, and 57.6 m. In addition, one piezometer at that site was installed in a separate borehole to a depth of 3 m in playa sediments.

These piezometer nests were initially installed in 1964 as part of a gas-injection tracer experiment that was done in 1967. For that test, about 38,000 m³ of air tagged with xenon-133 was injected into the unsaturated basalt at well GIN 8. Nest GIN 19 and GIN 9 are located 120 m and 500 m, respectively, from the injection well (Schmalz, 1969, fig. 5). During the injection, the xenon-133 tracer was detected in the piezometers and by downhole gamma radiation detectors at GIN 19 but not at GIN 9. Thus, atmospheric CFC's may have been introduced into the unsaturated zone at GIN 19 during that test.

During the 1979 sampling, CFC's were analyzed on-site by use of the system and methods described by Weeks and others, (1982). For the analyses, the chromatogram peak areas for the CFC's in air samples were assumed to be the same as the concentrations in the 1979 atmosphere (table 4). The subsurface concentrations, listed in table 7, were determined accordingly. The resulting profiles of concentration as a function of depth for CFC-11 might plausibly be explained by diffusion theory; however, the profiles for the two nests indicated that the effective diffusion coefficients were substantially different at the two sites. Also, the concentration from the 3-m piezometer at GIN 9 was only about 75 percent of that in the atmosphere. Such a phenomenon could be explained by the presence of a highly tortuous near-surface layer; however, an airpermeability test done at the site in 1969 indicated that the layer was indeed permeable to air. Thus, those results are not satisfactorily explained. In addition, the measured CFC-12 concentrations in the piezometers tapping the basalts at GIN 19 increased with depth. A possible explanation for this increase is that soil gas in the vicinity of GIN 19 was contaminated by CFC-12 in the air injected in 1967. The concentrations are greater than those of atmospheric air in 1967 (fig. 3), but CFC-12 could have been concentrated, for example, in the oil of the compressors used to inject the air. Because of these complications, no attempt was made to analyze these data at the time they were collected.

In 1991, samples were collected and analyzed as described above. These data indicate that the effects of nest construction, gas injection, and other possible complicating factors had dissipated. The resulting profiles of concentration as a function of depth indicate that ordinary gaseous diffusion is the dominant mechanism by which the CFC's reach depth in the unsaturated zone. Such a conclusion is of interest in dating ground water because ground water recharged after a long residence in the unsaturated zone would have an apparent CFC-based age that was much younger than the precipitation that produced the recharge. Fortunately, however, the effective diffusion rate for CFC-11 is enough slower than that for CFC-12 that the difference in

apparent ages for the two CFC's would be diagnostic of such slow recharge. In addition, a comparison of CFC-based ground-water ages with measured or estimated concentrations of CFC's in soil gas at the water table is useful for determining recharge mechanisms.

Confirmation that diffusion is the dominant transport mechanism at Birch Creek playa hence should be useful, as the theory could then be used to extend the observations to other areas. For this confirmation, the equation describing diffusion of a soluble, sorptive, nondegradable or nondecaying gas through a layered porous medium with an immobile liquid water phase (Weeks and others, 1982) was solved by use of the computer code described in that report. The equation, based on Fick's second-law describing this case of diffusion, is

$$\tau \theta_D D_{AB} \frac{\partial^2 C_A}{\partial x^2} = [\theta_D + \rho_w (\theta_T - \theta_D) K_w + \rho_s (1 - \theta_T) K_S] \frac{\partial C_A}{\partial t},$$

where r is tortuosity factor accounting for the added resistance to diffusion imposed by the structure of the porous medium (dimensionless),

 $\theta_{\rm D}$ is drained or gas-filled porosity (dimensionless),

D_{AB} is molecular diffusion constant for diffusion of gas A into gas B (cm²·s⁻¹),

C_A is concentration of gas A (mol·cm⁻³),

t is time (s),

 $\rho_{\rm w}$ is density of soil water (g·cm⁻³),

 $\theta_{\rm T}$ is total porosity (dimensionless),

 K_w is liquid-gas partitioning coefficient that describes the ratio of the concentration of substance A in solution to its concentration in the overlying gas phase under equilibrium conditions (mol·g-1 of water divided by mol·cm-3 of gas),

 ρ_s is particle density of granular material that makes up the solid matrix (g·cm⁻³),

 K_s is K_wK_d which is the gas-liquid-solid distribution product describing the ratio of the moles of substance A sorbed on the solid phase per unit mass of solid phase to the concentration of substance A in the soil atmosphere (cm³ of gas·g⁻¹ of solid).

For this study, the unsaturated-zone gases were assumed to be initially free of CFC's at the beginning of 1932, and the boundary condition at land surface was assumed to be that of a specified concentration. For each 30-day time step, land-surface CFC concentrations were interpolated from the estimated atmospheric concentrations on the basis of tabulated values of the data shown in figure 3. Each simulation was started in July 1932. The water table was assumed to be a no-diffusion boundary on the basis of the approximate 10,000-fold difference between gaseous and liquid diffusion rates.

For the simulations, each parameter except tortuosity was assumed to be known from other data. Relevant transport properties for CFC-11 and CFC-12 used in the simulation, as determined for the mean annual temperature and mean station barometric pressure at the site, are listed in table 8.

Table 8.--Molecular diffusion constant for the diffusion of gas A into gas B (D_{AB}), liquid partitioning coefficients (K_w), and sorptivity to geologic materials (K_s) of chlorofluorocarbon-11 and chlorofluorocarbon-12 are given.

[°C, degrees Celsius; kPa, kilopascals; cm, centimeters; s, seconds; g, grams]

	D _{AB} (10°C, 84kPa)	K _w (10°C, 84kPa)	K _s
Compound	$\mathrm{cm}^{2}\cdot\mathrm{s}^{-1}$	cm ³ .g ⁻¹	g.g-1
CFC-11	0.098	0.50	0
CFC-12	.107	.13	0

The diffusion coefficients were computed by use of the equations of Slattery and Bird (1958), as described by Weeks and others, (1982). Values of K_w , the liquid-gas partitioning coefficients, were computed from equation 6 of Warner and Weiss (1985). Values of K_s were interpreted from the fact that, in this study, ground water CFC-11 and CFC-12 ages are generally nearly identical, indicating that both CFC's are equally sorptive to the geologic materials existing in the vicinity of INEL. (This should be true only if the sorptivity of both compounds is zero or very small.) For the simulations, the two geologic media were divided into four layers -- two each for the playa sediments and for the basalts, as listed in table 9.

Drained porosity of 0.22 and total porosity of 0.39 for the playa sediments was assumed equal to the average values determined for 17 core samples, as cited by Schmalz (1969, p. 86). Air-filled and total porosities of the basalts are much more difficult to determine. An effective airfilled porosity of 0.05 was assumed; the same value was used by Robertson (1969) to analyze

the fate of the xenon-133 gas after the gas-injection test. A total effective porosity was assumed equal to 0.10, because Robertson (1974) used this value to analyze transport of solutes through saturated basalts in the southern part of INEL.

The 3-m depth boundary separating the upper and lower playa sediments is arbitrarily based on the depth of penetration of the shallow piezometers at the two nests. The boundary separating the upper and lower basalt layers is based on the fact that King (1968) determined, from tests on the well used to inject gas during the tracer test, that basalts present above the 40-m depth were much more permeable than those at greater depth. Although permeability to viscous flow and tortuosity to diffusive transport are not equivalent, the parameters are somewhat correlative.

The uppermost 3-m-thick layer was arbitrarily assigned a large tortuosity because of enhanced transport by barometric pumping (Weeks, 1978) and by the presence of animal burrows, root holes, worm holes, and desiccation cracks. In addition, the slightly higher than atmospheric concentrations measured at the 3-m depth indicate that CFC's sorbed on dry particles in the soil zone and were released into the deeper unsaturated zone when the soils became wet as a result of precipitation.

Table 9.--The total porosity (θ_T), the gas filled porosity (θ_D), and the tortuosity factor for the added resistance imposed by the structure of the porous medium (τ) are given as a function of depth and geologic material at Idaho National Engineering Laboratory [Depth interval below land surface in meters; --, not applicable]

Material	Depth interval	$ heta_{ m T}$	$ heta_{ m D}$	τ
Playa sediments	0-3			1.0
	3-17	0.39	0.21	0.3
Basalts	17-40			.14
	40-62	.10	.05	.09

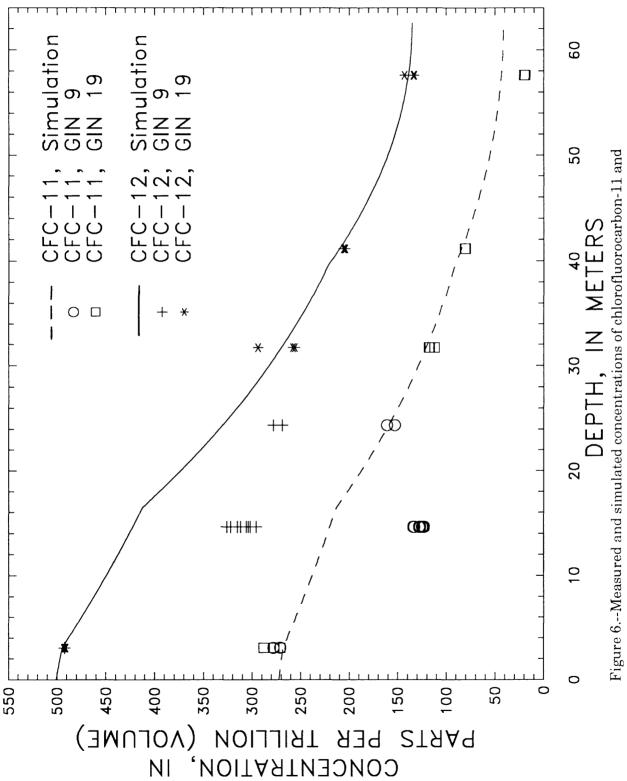
Tortuosities of each of the other layers were adjusted by trial and error to provide a plausible match to the measured concentrations of CFC-12. Once these tortuosities were determined (table 9), a simulation of CFC-11 depth profiles was made on the basis of the history of atmospheric buildup, free-air diffusion coefficient, and liquid-gas partitioning coefficient of CFC-11. Results of the simulations are shown along with measured concentrations in figure 6. The simulated profiles are in reasonable agreement for many, but not all, of the piezometers. In particular, the plot for the 16.5-m piezometer shows CFC-11 and CFC-12 concentrations that

are too low to be matched by any one-dimensional simulation that fits data for the other piezometers. A single tortuosity for the lower playa sediments allows a good match of both concentrations, indicating that local conditions in the vicinity of that piezometer impede diffusion.

Data from two other piezometers result in a mismatch between measured and simulated CFC-11 and CFC-12 concentrations. Measured CFC-11 concentrations for the 24.4 m piezometer at GIN 9 are matched quite well by the simulation, but the measured CFC-12 is depleted relative to its simulated value (fig. 6). The 1979 CFC-12 values also were low, as compared on a diffusion model basis, with respect to those for CFC-11. CFC-11 is more sorptive, soluble, and biodegradable than CFC-12; hence, the CFC-12 depletion relative to CFC-11 is difficult to explain. The CFC-11 concentration in the 57.6-m piezometer is depleted, on a diffusion-model basis, with respect to CFC-12. Quite possibly, this effect may be due to a highly tortuous diffusion path for both CFC-11 and CFC-12 in the basalts of relatively low permeability below a depth of 40 m, coupled with some residual CFC-12 contamination in the vicinity of the 57.6 m piezometer resulting from the 1967 gas-injection experiment.

Despite the various anomalies and the undoubted inadequacies of a one-dimensional model to describe diffusion in a highly heterogeneous system, gaseous diffusion quite plausibly explains most of the observed concentrations with depth in the unsaturated zone at TAN. These data, coupled with the measured CFC concentrations in ground water at INEL, provide some interesting insights on recharge mechanisms. As an example, if water had slowly recharged through the unsaturated zone at TAN, ground water having CFC concentrations in equilibrium with those measured in the 57.6-m piezometer would have an apparent CFC-11 date of recharge of 1963 and an apparent CFC-12 date of 1971. These dates contrast with those determined by analyses of ground-water samples obtained from the nearby P&W2 well of 1987 for CFC-11 and 1986 for CFC-12. In fact, nearly all of the water wells sampled in the INEL area that were not contaminated contained waters with nearly identical CFC-11 and CFC-12 ages (fig. 4, table 3), indicating that slow, uniform percolation through the unsaturated zone is not the dominant recharge mechanism in the vicinity of INEL.

The fact that CFC-11 in the 57.6-m piezometer is depleted relative to CFC-12 (based on results of a soil-gas diffusion model,) may result in a greater disparity in CFC-11 and CFC-12 ages than would ordinarily be the case. The CFC-11 model recharge date would be 1968 based on the simulation results shown in figure 6, only 3 years older than the CFC-12 date. Conversely, a diffusion model (not shown) that fits the 57.6-m piezometer CFC-11 data would yield a CFC-12 model date of 1966, again 3 years younger than the CFC-11 date. As a final comparison, the data for soil gas near the water table at the Glenn site in the Southern High Plains of Texas cited by Weeks and others, (1982) would have resulted in a CFC-11 model date of 1956 and a CFC-12 model date of 1960, a 4-year difference.



chlorofluorocarbon-12 with depth in the unsaturated zone at an installation near Test Area North at Idaho National Engineering Laboratory.

In conclusion, the soil-gas CFC concentrations at TAN are well explained by diffusion theory. Ground-water recharge occurring under traditionally assumed conditions of slow deep percolation would take on the diffusion-dominated CFC signature, the apparent result being (1) CFC water ages that are greater or equal to 20 years, and (2) CFC-11 based ages that are a few years greater than the CFC-12 based ages. This difference between apparent water ages based on CFC-11 and CFC-12 is as large as 7.5 years if the measured CFC concentrations at the base of GIN-19 are used (fig. 6) to calculate apparent water ages. The ground waters sampled near INEL indicate that the CFC-11 and CFC-12 ages are nearly identical. These observations indicate that ground-water recharge in the INEL area occurs episodically as slugs of water that do not equilibrate with the soil-gas atmosphere at the base of the unsaturated zone.

SUMMARY AND CONCLUSIONS

Detectable concentrations of chlorofluorocarbons (CFC's) were observed in the ground waters and unsaturated-zone gases from the Snake River Plain aquifer at the Idaho National Engineering Laboratory (INEL) in 1991. These results indicate that young ground waters were added at various locations to the older regional ground water within and outside the INEL boundaries. Calculated recharge ages of the waters were determined to be from 4 to more than 50 years on the basis of CFC concentrations.

Nitrogen-argon and CFC data from this study indicate that young ground water was added at various locations to the older regional ground water (greater than 50 years in age) within and outside the INEL boundaries. The Big Lost River, Birch Creek, the Little Lost River, and the Mud Lake-Terreton area seem to be major sources of recharge of the Snake River Plain aquifer at INEL. Most wells sampled this younger ground water.

The average nitrogen-argon recharge temperature of ground waters was about $9.7\pm1.3^{\circ}$ C, which is similar to the mean annual soil temperature of 9° C measured at INEL. This indicates that the aquifer was recharged at INEL and not at higher elevations where soil temperatures would be cooler than those at INEL. The concentrations of CFC's in the unsaturated-zone atmosphere near the top of the water table have a diffusion-dominated CFC-signature that was not present in the ground waters. These results indicate that recharge of the aquifer does not occur by slow deep percolation through the unsaturated zone. The mechanism of ground-water recharge that explains the N_2 -Ar and CFC data consists of (1) gas-water equilibration near or within the upper few meters of soil followed by (2) rapid movement of water through the basalt fractures to the water table without further water equilibration with the unsaturated-zone atmosphere.

Most ground water at INEL contains "natural" concentrations of CFC's with the exception of wells near the Radioactive Waste Management Complex, the Test Reactor Area, and areas south of the Idaho Chemical Processing Plant. The CFC data indicate that a large CFC-12 waste plume may originate from the Test Reactor Area. The areal extent of the CFC-12 waste plume may resemble the tritium-ground water plume; however, the CFC-12 plume seems to be larger.

The duration as well as rate of purging of a well when a water sample is collected can significantly affect the concentrations of CFC's and presumably other trace organics in the ground water. Faster purging rates resulted in higher CFC concentrations in one well. This increase in concentration was attributed to drawdown and introduction of younger and (or) contaminated waters with higher CFC concentrations.

Seven air piezometers were sampled near the Radioactive Waste Management Complex (RWMC). Contaminant concentrations of CFC's were present at all depths; however, the highest concentrations of CFC-11 and CFC-12 were observed in basalts between the 34-m and 73-m sedimentary interbeds. Concentrations of CFC's decreased above the 34-m interbed. The most likely source of CFC contamination is be the perched water-table that is present above the 73-m sedimentary interbed below the RWMC.

There may be a significant flux of CFC's from the unsaturated zone into the atmosphere near the RWMC. This is indicated by (1) the high concentrations of CFC-11 and CFC-12 measured in an air sample collected at this site and (2) the high concentrations present in the unsaturated zone at a depth of 4.6 m (CFC-11 and CFC-12 were 21 and 37 times the concentrations in 1991 air, respectively).

At Test Area North (TAN), the CFC concentrations in the unsaturated zone decreased from near atmospheric values (273 and 501 pptv for CFC-11 and CFC-12, respectively) at 3 m to 19 and 137 pptv for CFC-11 and CFC-12 at 57.6 m, respectively. The measured difference between apparent ages based on CFC-11 and CFC-12 is 7.5 years near the water table at TAN. These results are consistent with the diffusion of CFC's from the atmosphere into the unsaturated zone. The measured concentration of CFC's in ambient air at this site were similar to those present in the uncontaminated 1991 atmosphere.

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